1970; N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(22) The ideal conditions for rate comparisons are solutions of dilute acid in which the k_{obsd} values are directly dependent on [H$^+$]. However, the rates of many of the less reactive compounds are too low to be measured accurately under such conditions and are instead measured in stronger acids. Plots of log k_{obsd} vs. the acidity functions H_0 or H_R[21] have given reasonable straight lines, but the slopes of these plots are usually not unity. As a result conversion of the k_{obsd} values to k_2 by use of the relation $k_2 = k_{obsd}/h$ ($-$log $h = H$) gives different values of k_2 for different values of H. Extrapolations of k_{obsd} to lower values of acidity and then calculation of k_{obsd}/h still makes k_2 a function of the particular value of acidity chosen for the extrapolation. The extrapolation of the k_{obsd} vs. H plots can also introduce errors, either if the linear relation between the two is not exact within the experimentally observed range or if it changes outside the observed range. Plots of log k vs. H should have slopes of -1.0 at low acidities where the pH and H scales merge, but at higher acidities the magnitudes of these slopes usually are different from unity. In cases where the rates cannot be measured reliably at low acidity it cannot be determined where the scales merge, and the value of H to which k_{obsd} is extrapolated to determine k_2 is therefore rather arbitrary. Fortunately the values obtained by extrapolations to the region $H_0 = -1$ to $+1$ do not differ greatly. For example, k_2 values for ten substituted styrenes calculated by this method are larger for the higher acidity by factors of between 1.4 and 3.6.[12] These differences are significant but are small over the total range of substrate reactivity examined. The relationship between the acidity functions H_0 and H_R has been examined (A. J. Kresge, H. J. Chen, and Y. Chiang, *J. Chem. Soc., Chem. Commun.*, 969 (1972)) for hydrochloric and perchloric acids. It was found that in decreasingly acidic solutions down to values of about -1.0 these functions were linearly related, but that the relationship between the acidity functions was then curved to a value of about 1.0, at which point the functions each became equal to pH. Because of the extensive curvature at lower acidities it was concluded that linear extrapolations from higher acidities could not safely be carried beyond $H = 0$. The H_0 scale for sulfuric acid was also found to be almost equivalent to the pH scale at a value of about 1.0.

We have elected to use $H_0 = 0.0$ as a reasonable point of extrapolation based on its nearness to the region where the H_0 scale merges with pH, and its closer proximity to the range of experimental observations than some lower acidity. Because we have found little to choose between the use of H_0 or H_R functions we have based our extrapolations on the former. In those cases where the variation of the rate with acidity has not been determined we have used the relation $k_2 = k_{obsd}/h_0$ for the particular acidity studied. There is some inconsistency in k_2 values obtained this way; in particular the adoption of H_R as the standard for extrapolation, or a different acid strength as the point of extrapolation, would give different values of k_2. However, these variations are usually small compared to the overall range of reactivity examined, and the rates are very useful for comparative purposes, especially when the log k_{obsd} vs. H_0 slopes are near unity.

The most severe problem is with relatively unreactive compounds that have steep slopes of log k_{obsd} vs. H_0. The long extrapolations with a strong dependence of rate on acidity can cause large changes in rates relative to compounds with more gentle slopes. In the present series 1,3-butadiene (**28**) has a steeper slope than the other compounds, and the ratio k(**28**)/k(**27**) decreases from 26 at $H_0 = -5.27$ to 2.0 at $H_0 = 0$. This is the only extreme divergence in this group but illustrates that care is needed in the interpretation of small rate differences.

(23) (a) A. L. Henne, H. Chanan, and A. Turk, *J. Am. Chem. Soc.*, **63**, 3474 (1941); (b) L. F. Hatch, P. D. Gardner and R. E. Gilbert, *ibid.*, **81**, 5943 (1959); (c) Y. Pocker, K. D. Stevens, and J. J. Champoux, *ibid.*, **91**, 4199 (1969).

(24) (a) S. Winstein and L. Goodman, *J. Am. Chem. Soc.*, **76**, 4373 (1954); (b) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); (c) A. J. Ultée, Sr., *Recl. Trav. Chim. Pays-Bas*, **68**, 483 (1949).

(25) (a) A. A. Petrov, *Zh. Obshch. Khim.*, **13**, 102, 108 (1943); *Chem. Abstr.*, **38**, 329^8, 330^3 (1944); (b) L. F. Hatch and S. G. Ballin, *J. Am. Chem. Soc.*, **71**, 1039 (1949).

(26) C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(27) D. F. Shellhamer, D. B. McKee, and C. T. LEACH= *J. Org. Chem.*, **41**, 1972 (1976).

(28) Transmission coefficients have been discussed in slightly different contexts: J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, P 194; J. Hine, *J. Am. Chem. Soc.*, **81**, 1126 (1959).

(29) T. Inukai, *Bull. Chem. Soc. Jpn.*, **35**, 400 (1962).

(30) R. Baker, R. W. Bott, C. Eaborn and P. M. Greasley, *J. Chem. Soc.*, 627 (1964).

(31) A value for σ_p^+ for *p*-nitrophenyl of 0.06 has been determined from acetolysis of *p*-nitrophenylbenzyl tosylate at 69 °C: R. S. Bly, K.-W. Tse, and R. K. Bly, *J. Organometal. Chem.*, **117**, 35 (1976). This corresponds reasonably well to our value of -0.02.

(32) M. E. Bednas and D. S. Russell, *Can. J. Chem.*, **36**, 1272 (1958).

Acid-Catalyzed Hydrolysis of Vinyl Phosphates and Vinyl Acetates. The Substituent Effects of Diethyl Phosphoryloxy and Acetoxy Groups

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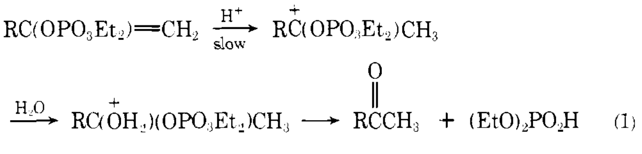
Abstract: The rates of hydration of diethyl α-substituted vinyl phosphates ($(EtO)_2PO_2CR{=}CH_2$, R = H, Me, c-Pr, and EtO) and α-substituted vinyl acetates ($AcOCR{=}CH_2$, R = c-Pr and EtO) in aqueous acid at 25 °C have been determined. The rates, solvent isotope effects, isotopic labeling studies, and acidity dependence of the rates are consistent with the $A_{SE}2$ mechanism of rate-determining protonation on carbon. Electrophilic substituent parameters (σ_p^+) have been determined for the groups diethyl phosphoryloxy and acetoxy as -0.13 and -0.06, respectively. Use of these substituent parameters allows the correlation of the rates of these vinyl esters by the equation $\log k_2 = \rho\Sigma\sigma_p^+ + C$. In addition the rates of 11 other vinyl esters available in the literature can also be included in the correlation.

Vinyl phosphates and vinyl acetates are two of the most important classes of alkenes. Vinyl phosphates are critical intermediates in a variety of metabolic pathways, and also are widely used as insecticides. Vinyl acetates are important synthetic intermediates and are extensively used in the preparation of polymers.

The hydrolysis mechanisms of vinyl phosphates and vinyl acetates have been established in some detail. By a variety of mechanistic criteria vinyl phosphates of the type $RC(OPO_3Et_2){=}CH_2$ have been shown to react in acid by the $A_{SE}2$ mechanism of rate-determining protonation of the double bond followed by addition of water with C–O bond cleavage (eq 1).[2-6] Vinyl acetates react through the same mechanism when



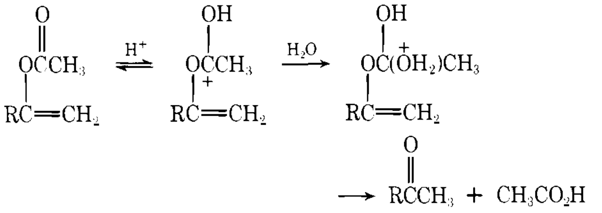
$$RC(OPO_3Et_2){=}CH_2 \xrightarrow[\text{slow}]{H^+} R\overset{+}{C}(OPO_3Et_2)CH_3 \xrightarrow{H_2O} RC(\overset{+}{O}H_2)(OPO_3Et_2)CH_3 \longrightarrow R\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + (EtO)_2PO_2H \quad (1)$$

the group R is electron donating, but when R is electron withdrawing react by the normal $A_{AC}2$ mechanism of ester hydrolysis (eq 2).[7,8]

Table I. Rates of Acid-Catalyzed Hydrolysis of Diethyl Vinyl Phosphates $RC(OPO_3Et_2)=CH_2$

R	H_2SO_4, M	H_2SO_4, %	H_0	H_R	k_{obsd}, s^{-1} [a]	Log k
Me	5.58[b]	41.6[c]	−2.53	−5.04	6.40×10^{-3} [d]	−2.194
(**54**)	4.89[b]	37.5[c]	−2.24	−4.36	2.78×10^{-3} [d]	−2.556
	4.23[b]	33.4[c]	−1.94	−3.72	1.40×10^{-3} [d]	−2.854
	4.23[b]				1.54×10^{-3} [e]	−2.812
	3.91[b]	31.3[c]	−1.80	−3.40	1.10×10^{-3} [e]	−2.959
	3.67[b]	29.7[c]	−1.68	−3.22	6.70×10^{-4} [d]	−3.174
	2.71[b]	22.9[c]	−1.25	−2.28	2.56×10^{-4} [d]	−3.592
	2.55[b]	21.8[c]	−1.15	−2.14	2.12×10^{-4} [e]	−3.674
	2.51[b]	21.5[c]	−1.12	−2.10	2.00×10^{-4} [e]	−3.701
			0.00[f]		1.72×10^{-5}	−4.764
H	12.09[c]	72.5[g]	−6.18	−12.18	1.37×10^{-2}	−1.863
(**53**)	11.22[c]	69.0[g]	−5.65	−11.26	5.58×10^{-3}	−2.253
	10.57[c]	66.3[g]	−5.27	−10.55	2.40×10^{-3}	−2.620
	9.82,[b] 9.81[c]	63.0[g]	−4.82	−9.68	1.17×10^{-3}	−2.932
	9.25[c]	60.5[g]	−4.52	−9.05	5.18×10^{-4}	−3.286
	8.10[c]	55.1[g]	−3.92	−7.72	1.67×10^{-4}	−3.777
	7.24[c]	50.8[g]	−3.45	−6.78	7.08×10^{-5}	−4.150
	6.81[c]	48.5[g]	−3.23	−6.32	3.36×10^{-5}	−4.474
			0.00[f]		6.05×10^{-8}	−7.218

[a] Average of at least two determinations, maximum deviation ±7%. [b] Determined by titration. [c] Interpolated from molarity vs. percentage tables. [d] From observation of acetone appearance. [e] From observation of alkene disappearance. [f] Extrapolated, using the lower acidity slope for **54**. [g] Determined from density measurements.


(2)

Despite these advances there have been fundamental unanswered questions regarding the reactivity of these compounds. Specifically it appeared from the previous work that the $A_{SE}2$ reactivity of the corresponding α-arylvinyl phosphates and acetates were similar.[2b] In view of our recent success in the correlation of alkene protonations with σ^+ substituent parameters[9] this led to the conclusion that these values for diethyl phosphoryloxy and acetoxy must be similar. However, the available information regarding the substituent effects of these groups was incomplete. Furthermore, the α-cyclopropylvinyl phosphate appeared to have a low reactivity in comparison to other derivatives.[10]

Correlations of infrared[11a] and ^{13}C NMR[11b] data allow calculation of σ_p^+ values for the p-acetoxy substituent of −0.03 and −0.06, respectively, and a value of −0.19 has been derived very recently from study of the chlorination of acetoxybenzene.[11c] A value of +0.05 may be derived for phosphoryloxy from the rate of protodesilylation of p-diethyl phosphoryloxytrimethylsilylbenzene[12] and the established[13] correlation of the rates of this reaction with σ^+ parameters. This indication that diethyl phosphoryloxy is apparently electron withdrawing seemed surprising in view of the fact that vinyl phosphates react by $A_{SE}2$ mechanisms.

Accordingly we have examined the reactivity of a number of other vinyl phosphates and acetates, and have made a separate determination of the substituent parameters for these groups.

Results

Diethyl vinyl phosphates **53–56** and vinyl acetates **60** and **61** were prepared as described in the Experimental Section. Of these compounds **55** and **56** had not been previously characterized but could be prepared using standard methods. The compounds are numbered in sequence with those of other papers in this series.[9]

$RC(OPO_3Et_2)=CH_2$		$RC(OAc)=CH_2$
53, R = H	**55**, R = c-Pr	**60**, R = c-Pr
54, R = Me	**56**, R = EtO	**61**, R = EtO

Rates of acid-catalyzed hydrolysis of **53** were measured by observing the disappearance of olefinic absorption at 196 nm in sulfuric acid solutions of various acidities. In the case of **54** the rates were followed both by the disappearance of olefinic absorption at 200 nm and also by observing the appearance of acetone absorbance at 262 nm with good agreement between rates obtained by the two methods. The rate data are collected in Table I. Plots of the log k_{obsd} vs. the acidity functions H_0[14] and H_R[15] are shown in Figures 1 and 2, respectively. Data for the corresponding vinyl acetates[7a] are included in the former case for comparison. The plot of log k vs. H_0 for **53** and **54** had slopes of −0.87 and −1.06 with intercepts of −7.22 and −4.91, respectively, and each had correlation coefficients of 0.998. The plot for **54** shows a slight break, but the four points at lowest acidity gave a slope of −0.95, intercept of −4.76, and a correlation coefficient of 1.000.

For comparison, values of −0.93 to −1.23 for slopes of log k vs. H_0 plots of $A_{SE}2$ reactions are cited in ref 7a. Plots of log k vs. H_R gave linear correlations with some scatter for both **53** and **54** over the entire range of acidities studied, with slopes of −0.43 and −0.51 and correlation coefficients of 0.999 and 0.998, respectively. The rates were extrapolated to $H_0 = 0.0$ to allow the calculation of second-order rate constants, using the low acidity slope in the case of **54**.

In the case of **55** rates were measured in hydrochloric acid by observing the decrease of the alkene maximum at 268 nm at a variety of temperatures and acid strengths as reported in Table II. A range of acid concentrations were examined at 54.8 °C and the correlations of the log k_{obsd} values were tested vs. the acidity functions H_0, H_R, and H_0 (55 °C) values (the acidity functions for HCl at 55 °C as measured by Gel'bshstein).[14] A good straight-line correlation with the H_0 values was obtained (Figure 3) with a slope of −1.16 whereas noticeably more scatter was observed for H_R or H_0 (55 °C).

The rates for **55** measured in 0.0496 M HCl at different temperatures gave activation parameters of $\Delta H^{\ddagger} = 22.0$ kcal/mol and $\Delta S^{\ddagger} = -13$ eu and a calculated rate at 25 °C of 5.34×10^{-7} s^{-1}. Division of this rate constant by the acidity function h_0 (0.0513 for 0.0496 M HCl) gives a second-order

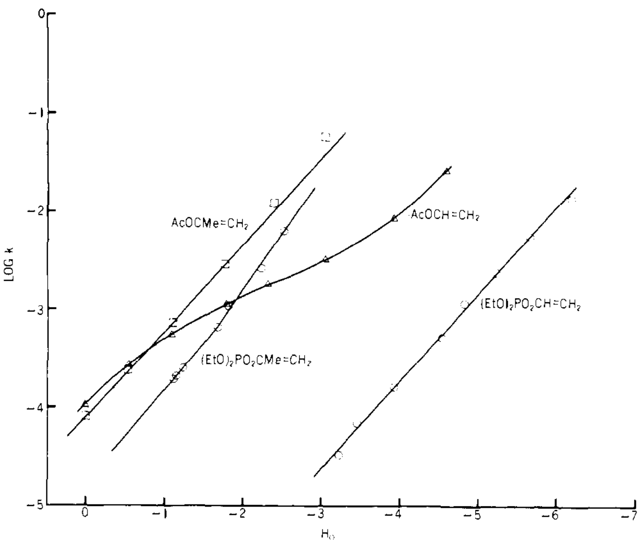


Figure 1. Hydration of vinyl esters.

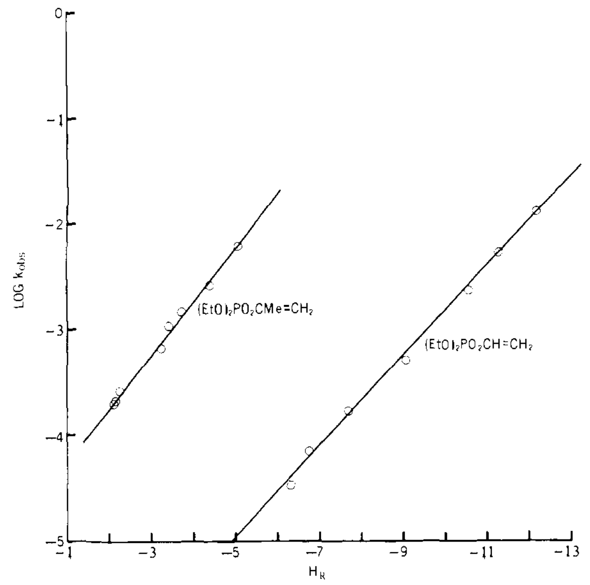


Figure 2. Hydration of vinyl phosphates.

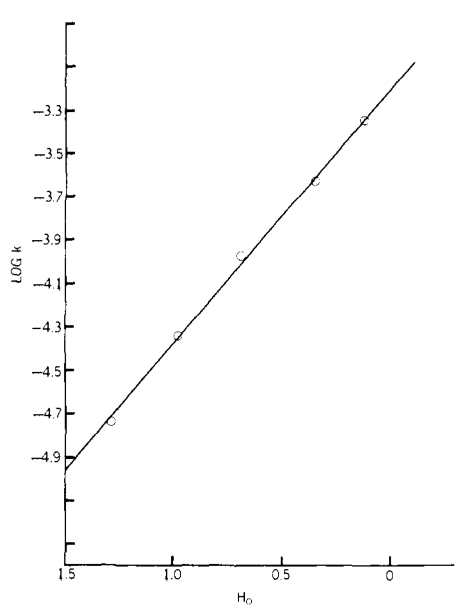


Figure 3. Hydration of c-PrC(OPO$_3$Et$_2$)=CH$_2$ (**55**) at 54.8 °C.

Table II. Hydrochloric Acid Catalyzed Hydrolysis of Cyclopropylvinyl Diethyl Phosphate, c-PrC(OPO$_3$Et$_2$)=CH$_2$ (**55**)

Temp, °C	[HCl], M	H_R	H_0	k_{obsd}, s^{-1}	Log k
84.9	0.0496	1.41	1.29	3.39×10^{-4}	−3.470
70.7	0.0496	1.41	1.29	7.66×10^{-5}	−4.116
54.8	0.0496	1.41	1.29	1.81×10^{-5}	−4.742
54.8	0.0992	1.10	0.98	4.57×10^{-5}	−4.340
54.8	0.198	0.74	0.69	1.07×10^{-4}	−3.971
54.8	0.397	0.35	0.35	2.36×10^{-4}	−3.627
54.8	0.595	0.07	0.12	4.52×10^{-4}	−3.345
25.0^a	0.0496	1.41	1.29	5.34×10^{-7}	
25.0	4.53^b (H_2SO_4)	−4.03	−2.08	1.63×10^{-3}	
25.0	4.53 (D_2SO_4)^c			1.14×10^{-3}	

[a] Calculated from data at higher temperatures, $\Delta H^{\ddagger} = 22.0$ kcal/mol, $\Delta S^{\ddagger} = -13$ eu, $k_2 = k_{obsd}/h_0 = 1.04 \times 10^{-5}$ M^{-1} s^{-1}. [b] 35.3% H_2SO_4, concentration determined by titration. [c] $k_{H_2SO_4}/k_{D_2SO_4} = 1.4$.

Table III. Rates of Acid-Catalyzed Hydrolysis of Ethoxyvinyl Diethyl Phosphate EtOC(OPO$_3$Et$_2$)=CH$_2$ (**56**)

H_2SO_4, M	H_0^{a}	h_0	k_{obsd}, s^{-1} $\times 10^3$	k_2, M^{-1} s^{-1}	
				k_{obsd}/h_0	$k_{obsd}/[H^+]$
0.0120	1.71	0.0195	0.724	0.0371	0.0302
0.0240	1.45	0.0355	1.36	0.0383	0.0283
0.0342	1.31	0.0490	1.88	0.0383	0.0276
0.0485	1.16	0.0692	2.55	0.0369	0.0263
0.0560	1.10	0.0794	3.00	0.0378	0.0268
0.0648	1.04	0.0912	3.39	0.0372	0.0262

[a] Sulfuric acid molarities converted to H_0 using the data of K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

rate constant of 1.04×10^{-5} M^{-1} s^{-1}. The observed rate constant at 25 °C for **55** in 4.53 M H_2SO_4 was 1.63×10^{-3} s^{-1} and division by the h_0 value of 115 for this acid gives a derived second-order rate constant of 1.42×10^{-5} M^{-1} s^{-1}. The greater magnitude of this rate constant from that derived in 0.0496 M HCl is expected, assuming that the magnitude of the slope of log k vs. H_0 is greater than unity in H_2SO_4 as it is in HCl.

The reaction product of **53** and **54** was determined to be diethylphosphoric acid by isolation as the dicyclohexylamine salt. The products of **55** were found to be cyclopropyl methyl ketone and diethylphosphoric acid, and the position of bond cleavage was established to be of the C–O bond by carrying out the hydrolysis in a mixture of dioxane and 3.5% ^{18}O-enriched water. The diethylphosphoric acid was isolated as the methyl ester and found to contain 0.1 ± 0.1% ^{18}O.

The hydrolysis of **56** was measured in dilute sulfuric acid, and the value of k_{obsd}/h_0 was constant (Table III).

The rates of hydrolysis of α-cyclopropyl vinyl acetate (**60**) were followed by observing the decrease in alkene absorption at 226 nm in sulfuric acid solutions and are presented in Table IV. The value of k_2 calculated from $k_2 = k_{obsd}/h_0$ was constant within the range of experimental error.

The rates of hydrolysis of α-ethoxyvinyl acetate (**61**) in acetic acid–sodium acetate buffer solutions were measured by following the disappearance of the alkene absorption at 226 nm and are reported in Table V. General acid catalysis was observed for this compound, and k_{H^+} was obtained by extrapolating the plot of k_{obsd} vs. [HOAc] at pH 4.34 to [HOAc] = 0. The derived values of k_{H^+} and $k_{[HOAc]}$ gave an excellent fit to k_{obsd} at other pH values (Table V).

Table IV. Sulfuric Acid Catalyzed Hydrolysis of Cyclopropylvinyl Acetate (c-PrCOAc=CH$_2$, **60**) at 25 °C

[H$_2$SO$_4$], M	% H$_2$SO$_4$	H_0	h_0	k_{obsd}, s^{-1}	$k_2 = k_{obsd}/h_0$, M^{-1} s^{-1}
0.1056[a]	1.03[b]	0.83	0.148	5.27×10^{-4}	3.56×10^{-3}
0.2117[a]	2.05[b]	0.54	0.288	1.03×10^{-3}	3.57×10^{-3}
0.3680[c]	3.53[a]	0.28	0.525	1.91×10^{-3}	3.63×10^{-3}

[a] Calculated from molarity vs. percentage tables. [b] Acid percentage determined from density measurements. [c] Determined by titration.

Table V. Rates of Hydrolysis of α-Ethoxyvinyl Acetate, EtOCOAc=CH$_2$ (**61**), in Acetic Acid Buffers, 25 °C

pH	[HOAc], M	[HOAc]/[NaOAc]	k_{obsd}, s^{-1} × 10^3	$k_{H^+}[H^+] + k_{HOAc}[HOAc]$, s^{-1} × 10^3 [a]
3.96	0.0784	6.27	3.79[b]	3.73
4.06	0.0759	5.06	3.31	3.42
4.21	0.0709	3.54	2.93	3.00
4.34	0.0330	2.64	1.60	1.62
4.34	0.0659	2.64	2.49	2.68
4.34	0.0989	2.64	3.78	3.79
4.34	0.1318	2.64	4.92	4.90
4.34	0.1648	2.64	6.08	6.02
4.34	0.1978	2.64	6.58	7.24
4.66	0.0509	1.27	2.06	1.93
4.85	0.0409	0.818	1.59	1.52

[a] Calculated from data at pH 4.34: $k_{H^+} = 9.85$ M^{-1} s^{-1}, $k_{HOAc} = 3.38 \times 10^{-2}$ M^{-1} s^{-1}. [b] This rate was unaffected by the addition of 0.1 M NaCl to the solution.

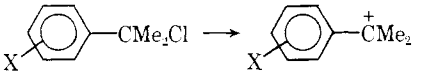
Table VI. Solvent Isotope Effects in the Hydrolysis of Esters R$_1$R$_2$C=CH$_2$ at 25 °C

R$_1$	R$_2$	Acid	k_{obsd}, s^{-1}	k_{H^+}/k_{D^+}
(EtO)$_2$PO$_2$	H	10.34 M D$_2$SO$_4$	9.27×10^{-4}	
53		10.34 M H$_2$SO$_4$[a]	2.04×10^{-3}	2.2
		9.04 M D$_2$SO$_4$	2.72×10^{-4}	
		9.04 M H$_2$SO$_4$[a]	4.67×10^{-4}	1.7
(EtO)$_2$PO$_2$	Me	3.05 M D$_2$SO$_4$	1.82×10^{-4}	
54		3.05 M H$_2$SO$_4$[a]	4.68×10^{-4}	2.6
(EtO)$_2$PO$_2$	c-Pr	4.53 M D$_2$SO$_4$	1.14×10^{-3}	
55		4.53 M H$_2$SO$_4$	1.63×10^{-3}	1.4
(EtO)$_2$PO$_2$	OEt	0.0715 M D$_2$SO$_4$	1.24×10^{-3}	
56		0.0715 M H$_2$SO$_4$[b]	3.65×10^{-3}	2.9
AcO	c-Pr	0.395 M D$_2$SO$_4$	6.31×10^{-4}	
60		0.395 M H$_2$SO$_4$[c]	2.09×10^{-3}	3.3

[a] Interpolated from the plot of log k_{obsd} vs. H_0. [b] Extrapolated from the plot of k_{obsd} vs. [H$_2$SO$_4$]. [c] Calculated from the direct dependence of k_{obsd} on h_0 (Table V) for this acidity (3.78% H$_2$SO$_4$, $H_0 = 0.24$, $h_0 = 0.575$).

The solvent isotope effects for the hydrolysis of **53–56** and **60** are given in Table VI.

To determine the σ^+ parameters for the acetoxy and phosphoryloxy substituents the meta- and para-substituted cumyl chlorides were prepared by HCl addition[16] to the corresponding isopropenylaryl esters (**1–4**). The rates of solvolysis of the chlorides (eq 3) were measured[17] in 90% acetone at 25



(3)

X = *p*-AcO (**5**)
m-AcO (**6**)
p-(EtO)$_2$PO$_2$ (**7**)
m-(EtO)$_2$PO$_2$ (**8**)

°C and the substituent constants were derived from the equation $\log k_x/k_H = \rho\sigma^+$ where ρ is -4.54.[18] The measured rate of cumyl chloride itself was in excellent agreement with that reported.[17] The rates and derived σ^+ values are listed in Table VIII.

The isopropenylaryl esters were prepared by acetylation[19a] or phosphorylation[19b] of the hydroxycumyl alcohols which underwent dehydration on distillation. *p*-Isopropenylphenyl acetate (**1**) seemed particularly prone to polymerization during this process. The cumyl alcohols were obtained from the addition of methylmagnesium iodide to the hydroxyacetophenones.[20]

Discussion

Derivation of Second-Order Rate Constants. For the comparison of trends in the rates it is useful to be able to compare compounds under the same conditions. For these acid-catalyzed reactions it is desirable to use second-order rate constants, but for the less reactive compounds it is necessary to use an acidity function besides the hydronium ion concentration to derive the second-order rate constants.

We previously found[2b] that the reactivities of diethyl α-arylvinyl phosphates in HCl solutions at different temperatures could be better correlated using the H_0 function than by H_R or H_0' (temperature corrected H_0 values). In the present case the correlation of log k is equally good vs. H_0 or H_R for **53**, whereas for **54** H_R gives a marginally better correlation (Figures 1 and 2). Extrapolation of the log k_{obsd} vs. acidity functions plot to $H = +1.0$ and division of k_{obsd} by the corresponding function h ($-\log H = h$) of 0.10 gave second-order rate constants (M^{-1} s^{-1}) for **53** of 7.85×10^{-8} and 2.82×10^{-7} for H_0 and H_R, respectively, whereas the corresponding values for **54** were 2.02×10^{-5} and 5.12×10^{-5}, respectively. Clearly the choice of the acidity function used as a basis of comparison will affect the exact k_2 values, but there is little to choose between the utility of H_0 and H_R to correlate the rates. It has been reported[21] that for *trans*-cyclooctene hydration log k is linear in H_R, whereas for phenyl vinyl ether log k is linear in H_0. We have found[9b] that for 2-substituted 1-cyclopropylalkenes there is little difference in the ability of H_0 and H_R to correlate the data. Lacking good reasons for a choice we have arbitrarily used H_0 for calculating k_2 values, and have chosen $H_0 = 0.0$ as the point of extrapolation.

For diethyl α-cyclopropylvinyl phosphate (**55**) k_2 values at 25 °C were obtained both by extrapolating rates for 0.0496 M HCl at higher temperatures to 25 °C and by measuring the rate at 25 °C in 4.53 M H$_2$SO$_4$. The k_2 values (M^{-1} s^{-1}) of 1.04×10^{-5} and 1.42×10^{-5}, respectively, were in close enough agreement to lend further confidence to the methods for deriving the second-order rate constants. Likewise for diethyl α-phenylvinyl phosphate (**57**) we derived[2b] a k_2 value of 1.31×10^{-5} for measurements in 1 M HCl, whereas the rates of Bunton[4] for 0.1 M HClO$_4$ lead to a value of 1.15×10^{-5}.

A comparison of the rate ratio $k_{obsd}(\mathbf{54})/k_{obsd}(\mathbf{57})$ reveals a continuous variation with acidity from 1.3 in 1.5 M H$_2$SO$_4$ to 0.82 in 4 M acid. This arises from the different slopes of the

Table VII. Comparative Second-Order Rate Constants for Acid-Catalyzed Hydrolysis of Vinyl Phosphates and Acetates ($RC(OR')=CH_2$) at 25 °C

	$R' = (EtO)_2PO$				$R' = Ac$				kAc)/
R	No.	k_2	Ref	k_{rel}	No.	k_2	Ref	k_{rel}	$k(EtO)_2PO$
H	**53**	6.05×10^{-8}	*a*	1.0	**58**	8×10^{-7}	*f*	1.0	13
Me	**54**	1.72×10^{-5}	*a*	284	**59**	5×10^{-5}	*f*	62	2.9
c-Pr	**55**	1.04×10^{-5}	*b*	172	**60**	3.59×10^{-3}	*g*	4.5×10^3	345
EtO	**56**	0.0376	*c*	6.2×10^5	**61**	9.85	*h*	1.2×10^7	260
Ph	**57**	1.11×10^{-5}	*d*	183[e]	**62**	9.9×10^{-6}	*i*	12[j]	0.89

[a] Table I. [b] Table II. [c] Table III. [d] Reference 4 (k_{obsd} (0.100 M $HClO_4$, $h_0 = 0.104$) = 1.15×10^{-6}, $k_{obsd}/h_0 = 1.11 \times 10^{-5}$). [e] A ratio of 2.3 for **54**/**57** in 0.1 M HCl in 40/60 $EtOH/H_2O$ at 85 °C was reported in ref 5, as compared to our value of 1.5. [f] Estimates from ref 7a. [g] Table IV. [h] Table V. [i] Calculated by multiplying k_2 for p-TolC(OAc)=CH_2 (Table X) by the PhC(OAc)=CH_2/p-TolC(OAc)=CH_2 rate ratio of 0.232 at $H_0 = -2.55$, where both compounds appear to react by the $A_{SE}2$ path.[7a] [j] Estimated in ref 7a by a slightly different comparison to be 40.

Table VIII. Rates of Solvolysis of Substituted Cumyl Chlorides ($XPhCMe_2Cl$) in 90% Acetone at 25 °C

X	k_1, s^{-1} [a]	σ^{+} [b]	k_{rel}	Log k_{rel}
H	1.237×10^{-4}	0.0	1.000	
p-$(EtO)_2PO_2$	4.69×10^{-4}	−0.127	3.79	0.579
m-$(EtO)_2PO_2$	4.55×10^{-6}	0.316	0.0368	−1.434
p-AcO	2.434×10^{-4}	−0.0648	1.968	0.294
m-AcO	7.06×10^{-6}	0.274	0.0571	−1.243

[a] Each value is the average of two or more runs. Maximum deviations were ±4% except for m-AcO which gave an infinity titration greater than 100%, apparently due to partial hydrolysis of the acetoxy group. The reported rates in this case, calculated by Swinbourne and Guggenheim procedures, had a maximum deviation of ±6%. [b] $\sigma^+ = (-\log k_x/k_H)/4.54$.

log k_{obsd} vs. H_0 plots (−1.06 for **54** and −1.18 for **57**[4]) and this medium effect on the rate ratio provides an explanation for why the ratio of k_2 values (1.55, Table VII) differs from the reported[3] value of 0.4 for k_{obsd} $(MeO)_2PO_2CMe=CH_2/k_{obsd}$ $(MeO)_2PO_2CPh=CH_2$ in 60/40 dioxane/H_2O 1.98 M in $HClO_4$.

The plot of k_{obsd} vs. H_0 for the protonation of **57** derived from the rates of Bunton and Robinson[4] for 1.5-4 M H_2SO_4 solutions gives a good straight line of slope −1.18. However, the k_2 value derived from extrapolation of this line to $H_0 = 0.0$ is 6.5×10^{-6}, half the value derived above from data of the same authors for 0.1 M $HClO_4$ and our own data in 1 M HCl. It seems that in more dilute H_2SO_4 the slope of log k vs. H_0 would be less steep for **57**, as we noted for **55**.

It appears, therefore, that the derived k_2 values are useful for the analysis of large differences in substituent effects but that small variations may well arise from medium effects and the methods for calculating the k_2 values. In cases where the substrates are so unreactive that rates cannot be measured in solutions of low acidity we have extrapolated the rates to $H_0 = 0$. The selection of this acidity is rather arbitrary, but as explained in more detail elsewhere,[9c] this seems a better choice than a lower acidity as the former is nearer the experimental range, and because the slopes of log k vs. H_0 may well change at acidities less than $H_0 = 0$.

Mechanism of the Hydration Reactions. The results support the $A_{SE}2$ mechanism of hydrolysis (eq 1) for compounds **53–56** and **60** and **61.** The correlations of log k with H_0 values, the solvent isotope effects, and the isotope labeling study and activation parameters for **55** are all in agreement with the usual criteria for this mechanism.[2-4,7] An isotope labeling study reported[3] for a close analogue of **54**, namely, $(MeO)_2PO_2$-$CMe=CH_2$, also supports this mechanism.

The isolation of the dicyclohexylamine salt of diethylphosphoric acid from the reaction of diethyl vinyl phosphate shows that even for this compound protonation on the double bond takes precedence over hydrolysis of the ethyl groups and the reaction proceeds as in eq 1. This is in agreement with the results of our study of the reactivity of triethyl phosphate,[22] whose second-order rate of acid-catalyzed hydrolysis at 25 °C may be estimated to be less than 10^{-8} M^{-1} s^{-1}. Thus if the ethyl groups in diethyl vinyl phosphate (**53**) and triethyl phosphate have the same reactivity attack at the vinyl group in the former compound would be at least 10 times faster than hydrolysis of the ethyl groups.

Substituent Parameters for Diethyl Phosphoryloxy and Acetoxy. The magnitudes of the σ_p^+ values of −0.13 and −0.06 for these groups are quite small in comparison to the values for OH (−0.92) and OMe (−0.78).[18] The inductive withdrawal by the carbonyl and phosphoryl groups, and the resonance interaction in the former, have reduced the cation stabilizing ability of the phenolic oxygens as measured by the σ_p^+ parameters by 85–93%. Comparison with the previously determined values for these substituents cited above (−0.03, −0.06, and −0.19 for acetoxy and +0.05 for phosphoryloxy)[11,12] shows agreement with the general magnitude of the values obtained by the cumyl chloride hydrolysis. The cumyl chloride rates agree with unpublished data of Isaacs.[11c]

Swain and Lupton[23] have proposed that the effects of substituents arise from only two independent factors, namely, field and resonance effects, and have suggested that any substituent constant for a given group is a linear function of any other two substituent functions for that group. On this basis they have calculated σ_p^+ constants using σ_m and σ_p constants for a variety of groups for which σ_p^+ constants have not been experimentally determined. Their calculated value of 0.18 for σ_p^+ of acetoxy is in very modest agreement with our experimental value, but falls within the limits of agreement of other substituents in their set.

The measured σ_m^+ constants should be similar to the values of σ_m for the same groups. A value of 0.39 for σ_m has been reported for acetoxy,[24] but apparently no value of σ_m has been reported for diethyl phosphoryloxy. However, σ_m^+ for the latter group is available from protodetrimethylsilylation as 0.25,[12,13] and for the former group from chlorination of p-acetoxyacetanilide as 0.26.[11c] Our measured values of 0.32 for diethyl phosphoryloxy and 0.27 for acetoxy are in good agreement with these values.

Correlation of the Alkene Hydrations. The use of the σ_p^+ parameters for the acetoxy and diethyl phosphoryloxy substituents determined from the cumyl chloride solvolyses allows the ten vinyl acetates and phosphates listed in Table IX to be correlated by our previously derived equation[9]

$$\log k_2 = -12.3\Sigma\sigma_p^+ - 10.1 \quad (4)$$

These points (triangles, **53–62**) are added to the correlation line already published[9] in Figure 4. In general the fit of the

Table IX. Rates of Hydration at 25 °C of Vinyl Esters $RC(OR')=CH_2$ in Aqueous Acid[a]

No.	R	σ_p^+	R	σ_p^+	$\Sigma\sigma_p^+$	k_2, $M^{-1}\ s^{-1}$	Log k_2
53	H	0.0	$(EtO)_2PO$	−0.13	−0.13	6.05×10^{-8}	−7.218
54	Me	−0.31	$(EtO)_2PO$	−0.13	−0.44	1.72×10^{-5}	−4.764
55	c-Pr	−0.47	$(EtO)_2PO$	−0.13	−0.60	1.04×10^{-5}	−4.983
56	EtO	−0.72	$(EtO)_2PO$	−0.13	−0.85	0.0376	−1.425
57	Ph	−0.18	$(EtO)_2PO$	−0.13	−0.31	1.11×10^{-5}	−4.955
58	H	0.0	Ac	−0.06	−0.06	8×10^{-7}	−6.097
59	Me	−0.31	Ac	−0.06	−0.37	5×10^{-5}	−4.301
60	c-Pr	−0.47	Ac	−0.06	−0.53	3.59×10^{-3}	−2.445
61	EtO	−0.72	Ac	−0.06	−0.78	9.85	0.993
62	Ph	−0.18	Ac	−0.06	−0.24	9.9×10^{-6}	−5.004

[a] The σ_p^+ values are from the compilation in ref 9a. That for *p*-c-Pr has been slightly revised; see footnote *a*, Table VII, ref 9b.

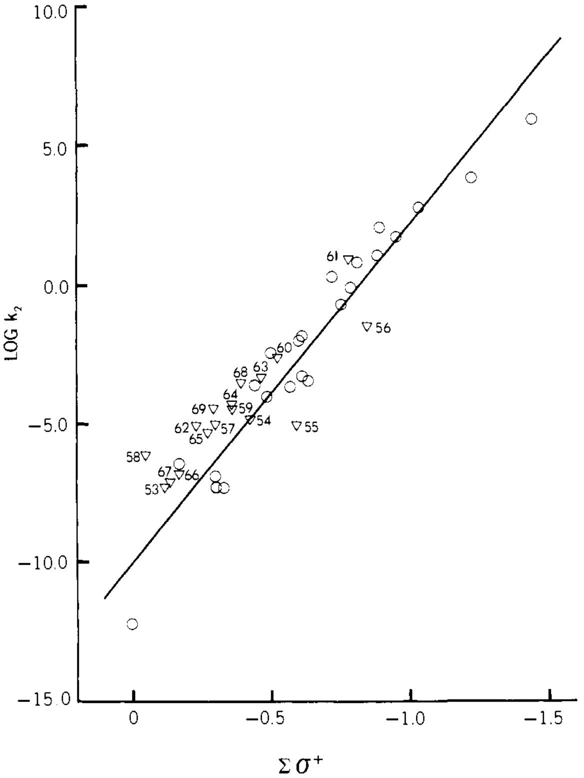


Figure 4. Correlation of log *k* hydration of vinyl esters (∇) vs. σ_p^+ parameters.

points to the previously established correlation line is quite satisfactory. The agreement of the data for these two classes of vinyl esters lends added support and confidence to the use of eq 4 to correlate the reactivity of alkenes in acid-catalyzed hydration, and also lends further support to the $A_{SE}2$ mechanism for reaction of these compounds.

Although the broad picture of the reactivity appears to be adequately accounted for, there are certain anomalies in the individual reactivities. In particular the rate constants for the α-cyclopropylvinyl and α-ethoxyvinyl phosphates **55** and **56** are factors of 340 and 260 times less reactive than the corresponding acetates, and these phosphates show corresponding deviations well below the correlation line in Figure 4. The acetates are very close to the expected reactivity. It was recognized previously[10] by one of us that the cyclopropylvinyl phosphate had an unusually low reactivity. At that time this was attributed[10] to a strong stabilizing effect of the phosphoryloxy leveling the cation stabilizing effect of the cyclopropyl. As a result of our further work this explanation is no longer acceptable. Phosphoryloxy is not an especially strong electron-donating group, as evidenced by the low magnitude of σ_p^+ for this substituent. Furthermore, leveling or saturation effects,[25] if they occur at all in alkene hydrations, are relatively modest, as evidenced by the general lack of curvature in Figure 4.[9a]

The mechanistic evidence for **55** and **56** strongly favors the $A_{SE}2$ path in each case, and other examples of these structural types appear well behaved in that they are accounted for by the correlation. It may be that there is an unusual ground state stabilization in these derivatives, but it is not obvious that this would be so. Another possibility is that conformational problems arise in the cation intermediate and the transition state leading to it which reduce the ability of the substituents to conjugate. The substituents involved, cyclopropyl and ethoxy, do have geometric requirements for the most favorable arrangement for electron donation, and the phosphoryl group is quite bulky. Conformational problems might have also been anticipated with the α-phenylvinyl phosphate but are not apparent. It may be that the conformational effects do intervene but are less noticeable because the total resonance effect is not as significant for phenyl as for cyclopropyl and ethoxy. Thus steric crowding in the transition states for hydration causing a decrease in the conjugative stabilization by the substituents is a plausible candidate for the lower than anticipated reactivities for **55** and **56**, but at present there is no proof that this is true.

It was also possible to use the method we have developed[9c] for the correlation of the rate of aryl substituted styrenes to include five arylvinyl phosphates **63**–**67** and two arylvinyl acetates **68** and **69** in the correlation. The data are summarized in Table X and the points are included in Figure 3. It may be seen that these compounds readily fit into the correlation.

Experimental Section

^1H NMR spectra were run using a Varian T-60 instrument with the solvents indicated and Me_4Si as an internal standard. Elemental analyses were by the Galbraith Laboratories.

Acid solutions were prepared by diluting concentrated reagent with water. Acid strengths were determined by titration and converted to percentages using standard tables[26] unless noted otherwise. Concentrated D_2SO_4 was obtained from Aldrich-Diaprep and was diluted with D_2O to give solutions of various strengths.

Kinetics of the alkene hydrations were run using Cary 14 and 118 and Unicam 1800 spectrophotometers with thermostated cell compartments, and were followed by monitoring the ultraviolet absorption in 1-cm cells. The decrease at the absorption maxima of the reactant was observed for **53** (196 nm), **54** (200 nm), and **55** (268 nm). The appearance of acetone at 262 nm was also observed for **54**. The other alkenes were observed on the shoulders of the absorption bands at 240 (for **56**) and 226 nm (for **60** and **61**). Each rate reported is the average of at least two runs. Alkene (5×10^{-3} mmol) was injected with a syringe into 3 mL of acid solution contained in the cell maintained at 25 °C, the cell was shaken, and the disappearance of the alkene absorption of the resulting 1.5×10^{-3} M solution was followed. For **54** some of the runs were carried out using 30 μL (0.15 mmol) of phosphate to give 0.05 M solutions and the appearance of acetone at 262

Table X. Rates of Hydration at 25 °C of α-Arylvinyl Esters $ArC(OR){=}CH_2$ in Aqueous Acid

No.	Ar	$\sigma_p^{+\,a}$	R	σ_p^+	$\Sigma\sigma_p^+$	k_2, $M^{-1}\,s^{-1}$ [b]	Log k_2
63	*p*-Anis	−0.34	$(EtO)_2PO$	−0.13	−0.47	5.70×10^{-4}	−3.24
64	*p*-Tol	−0.24	$(EtO)_2PO$	−0.13	−0.37	5.77×10^{-5}	−4.24
65	*p*-BrPh	−0.15	$(EtO)_2PO$	−0.13	−0.28	5.93×10^{-6}	−5.23
66	*m*-O_2NPh	−0.05	$(EtO)_2PO$	−0.13	−0.18	1.83×10^{-7}	−6.74
67	*p*-O_2NPh	−0.02	$(EtO)_2PO$	−0.13	−0.15	8.46×10^{-8}	−7.07
68	*p*-Anis	−0.34	Ac	−0.06	−0.40	3.33×10^{-4} [b]	−3.48
69	*p*-Tol	−0.24	Ac	−0.06	−0.30	4.27×10^{-5} [c]	−4.37

[a] Calculated from the formula $\sigma_p^+(XPh) = 0.2\ \sigma^+(X) + \sigma_p^+(Ph)$, ref 9c. **63–67**, ref 2b; **68**, **69**, ref 7b. [b] The observed rate at $H_0 = 0.02$ was assumed to be solely due to the $A_{SE}2$ mechanism so k_2 taken equal to k_{obsd}/h_0 for this acidity. [c] The observed rate at $H_0 = -1.74$ was assumed to be solely $A_{SE}2$ so k_2 was obtained by multiplying k_2 for **68** by the **69**/**68** rate ratio at $H_0 = -1.74$.

nm was monitored. The hydrolysis of **55** above room temperature was followed for 10^{-4} M solutions at 268 nm by the ampule technique. The decrease in absorption of **56** was followed at 240 nm for a 6×10^{-3} M solution, and **60** and **61** were observed at 226 nm, using 10^{-2}–10^{-3} M solutions.

The kinetics of hydrolysis of the cumyl chlorides were measured in 90% acetone at 25 °C by the reported[17] procedure.

Reaction Products. Diethyl vinyl phosphate (**53**, 1.17 g, 6.5 mmol) was dissolved in 30 mL of 63% H_2SO_4 and left for 2 h at 25 °C (10 half-lives). The mixture was subjected to continuous liquid–liquid extraction with CH_2Cl_2 for 48 h. Evaporation of the CH_2Cl_2 left 0.97 g (6.3 mmol, 97%) of diethylphosphoric acid with the same NMR spectrum as an authentic sample. This residue was dissolved in 20 mL of CH_2Cl_2 and reacted with 1.4 g of dicyclohexylamine. After 24 h the precipitate was collected by filtration and recrystallized from CH_2Cl_2 to give 1.01 g (2.9 mmol, 45%) of dicyclohexylammonium diethyl phosphate: mp 140–142 °C (lit.[27b] 140–140.5 °C). Anal. Calcd for $C_{16}H_{34}NO_4P$ (335.42): C, 57.29; H, 10.22; N, 4.18. Found: C, 57.45; H, 10.10; N, 4.20. Found for an authentic sample: C, 57.27; H, 10.00; N, 4.17. The same salt was isolated by the corresponding reactions of diethyl α-methylvinyl phosphate (**54**).

The product analysis of the hydrolysis of diethyl α-cyclopropylvinyl phosphate was carried out using an HCl solution with 3.5% ^{18}O-labeled H_2O as described previously.[2a] Mass spectral analysis of the isolated diethyl methyl phosphate derived from diazomethane methylation of the product diethylphosphoric acid revealed 0.1 ± 0.1% ^{18}O incorporation. In a separate experiment in ordinary water cyclopropyl methyl ketone was the only volatile product detected by VPC.

Diethyl vinyl phosphate (**53**)[28] was prepared from the reaction of monochloroethylene carbonate[29] with triethyl phosphite: NMR (CCl_4) δ 1.32 (t, 6, J = 7 Hz, Me), 4.08 (octet, 4, $J_{P\text{-}H}$ = 9 Hz, $J_{H\text{-}H}$ = 7 Hz, OCH_2), 4.5–4.8 (m, 2, $C{=}CH_2$), 6.55 (m, 1, $C{=}CHO$) (the vinyl resonances have been assigned in ref 28 and 30b); UV (H_2O) λ_{max} 196 nm.

Diethyl α-methylvinyl phosphate (**54**)[31] was prepared by the Perkow reaction of bromoacetone[32] with triethyl phosphite: NMR[30] (CCl_4) δ 1.30 (t, 6, J = 7 Hz, 2 Me), 1.90 (s, 3, $C{=}CMe$), 4.08 (octet, 4, $J_{P\text{-}H}$ = 9, $J_{H\text{-}H}$ = 7 Hz, OCH_2), 4.46 (t, 1, J = 1 Hz, $C{=}CH$), 4.68 (t, 1, J = 1 Hz, $C{=}CH$); UV (H_2O) λ_{max} 200 nm.

Diethyl α-cyclopropylvinyl phosphate (**55**) was prepared by the general procedure of Ireland[33] and Borowitz.[34] Cyclopropyl methyl ketone (8.4 g, 0.1 mol) was added dropwise to 4 g of sodium hydride (0.17 mol, prewashed with pentane) in 200 mL of dry DME at 0 °C. The solution was stirred for 15 h at room temperature, diethyl chlorophosphate (29.4 g, 0.17 mol) was added, and the solution was refluxed for 9 h, poured onto ice, and extracted three times with pentane. The extracts were dried and after removal of the solvent on the rotary evaporator the residue was distilled to give **55** (7.5 g, 0.034 mol, 34%): bp 58–60 °C (0.02 Torr); NMR (CCl_4) δ 0.5–0.8 (m, 4, c-Pr), 1.30 (t, 6, $J_{H\text{-}H}$ = 7, $J_{P\text{-}H}$ = 1 Hz, Me), 1.3 (m, 1, c-Pr concealed), 4.04 (octet, 4, $J_{H\text{-}H}$ = 7, $J_{P\text{-}H}$ = 8 Hz, OCH_2), 4.43 (t, 1, J = 2 Hz, $C{=}CH$), 4.73 (t, 1, J = 2 Hz, $C{=}CH$); UV (H_2O) λ_{max} 192 nm (ϵ 8600), 268 (302). The specific electronic transition causing this unique long wavelength band has not been identified.

Anal. Calcd for $C_9H_{17}O_4P$ (220.21): C, 49.09; H, 7.78. Found: C, 49.16; H, 7.96.

When the preparation of **55** via the Perkow reaction[31] of cyclopropyl chloromethyl ketone[35] and triethyl phosphite was carried out the product mixture appeared by NMR to consist of a 47:53 mixture of **55** and **diethyl 2-oxo-2-cyclopropylethylphosphonate** (c-PrCO-$CH_2PO_3Et_2$, **9**). Distillation gave **9** as the last fraction: bp 90 °C (0.1 Torr); NMR (CCl_4) δ 0.6–0.9 (m, 4, c-Pr), 1.30 (t, 6, J = 7 Hz, Me), 2.2 (m, 1, CHCO), 3.09 (d, 2, $J_{P\text{-}H}$ = 22 Hz, CH_2P), and 4.04 (octet, 4, $J_{P\text{-}H}$ = 8, $J_{H\text{-}H}$ = 7 Hz, OCH_2).

Anal. Calcd for $C_9H_{17}O_4P$ (220.21): C, 49.09; H, 7.78. Found: C, 48.70; H, 7.95.

Diethyl α-ethoxyvinyl phosphate (**56**) was prepared by the addition to 1.5 g (0.021 mol) of ethoxyacetylene (Chemical Samples Co.) in CH_2Cl_2 with 0.03 g of $Hg(OAc)_2$ and 1 g (7 mmol) of diethylphosphoric acid (Aldrich) in CH_2Cl_2 at −30 °C. The product was distilled at 103 °C and 3 Torr: NMR (CCl_4) δ 1.51 (t, 6, J = 7 Hz, $POCH_2CH_3$), 1.53 (t, 3, J = 7 Hz, $COCH_2CH_3$), and 3.5–4.4 (m, 8, $C{=}CH_2$ and 3 OCH_2); yield 0.75 g (3 mmol, 40%); UV (H_2O) λ_{max} 203 nm.

In a previous preparation **56** was an unisolated intermediate but reacted further with excess diethylphosphoric acid.[36]

Anal. Calcd for $C_8H_{17}O_5P$ (224.19): C, 42.86; H, 7.64. Found: C, 42.80; H, 7.65.

Cyclopropylvinyl acetate (**60**)[37] was prepared from toluenesulfonic acid catalyzed interchange of cyclopropyl methyl ketone and isopropenyl acetate,[37] and showed λ_{max} (H_2O) 192 nm (ϵ 3.3×10^4).

α-Ethoxyvinyl acetate (**61**)[38] was prepared by the mercuric acetate catalyzed addition of acetic acid to ethoxyacetylene[38] and was separated from the by-product acetic anhydride by gas chromatography (2 m × 6 mm OV-17 on Chromosorb W, column 100 °C, 50 ml/min He): NMR (CCl_4) δ 1.34 (t, 3, J = 7 Hz, CH_2CH_3), 2.09 (s, 3, CH_3CO), 3.68 (m, 2, $C{=}CH_2$), and 3.83 (quartet, 2, OCH_2); no λ_{max} >192 nm was observed for this compound.

Preparation of Cumyl Chlorides. Addition to *m*- and *p*-hydroxyacetophenones of methylmagnesium iodide gave *m*-hydroxycumyl alcohol (NMR (Me_2SO-d_6) δ 1.46 (s 6, Me_2), 4.90 (s, 1, OH), and 6.9 (m, 4, Ar)) and *p*-hydroxycumyl alcohol (NMR (C_3D_6O) δ 1.40 (s, 6, Me_2), 4.68 (s, 1, OH), and 6.64 and 7.33 (each d, 2, A_2B_2 of Ar)), respectively. The phenols were directly esterified by acetic anhydride[19a] or diethyl chlorophosphate with triethylamine[19b] and distilled to give the isopropenylaryl esters: *p*-isopropenylphenyl acetate (**1**)[20] (bp 120 °C (10 Torr); NMR (CCl_4) δ 2.12 (broad s, 3, vinyl Me), 2.25 (s, 3, MeCO), 5.06 and 5.31 (broad singlets, each 1, $C{=}CH_2$), and 7.21 (quartet, 4, aryl)); *m*-isopropenylphenyl acetate (**2**)[19a] (bp 120 °C (10 Torr); NMR ($CDCl_3$) δ 2.07 (broad s, 3, vinyl Me), 2.22 (s, 3, MeCO), 5.04 and 5.31 (broad singlets, each 1, $C{=}CH_2$), and 7.2 (m, 4, aryl)); diethyl *p*-isopropenylphenyl phosphate (**3**) (bp 165 °C (0.02 Torr); NMR (CCl_4) δ 1.33 (t, 6, $J_{H\text{-}H}$ = 7, $J_{P\text{-}H}$ = 1 Hz, 2 Me), 2.11 (d, 1, J = 1.5 Hz, vinyl Me), 4.22 (m, 4, 2, OCH_2), 5.02 (quartet, 1, J = 1.5 Hz, vinyl H), 5.29 (broad singlet, 1, vinyl H), and 7.26 (quartet, 4, aryl)); and diethyl *m*-isopropenylphenyl phosphate (**4**) (bp 138 °C (0.02 Torr); NMR (CCl_4) δ 1.32 (t, 6, $J_{H\text{-}H}$ = 7, $J_{P\text{-}H}$ = 1 Hz, 2 Me), 2.10 (d, 3, J = 1.5 Hz, vinyl Me), 4.22 (m, 4, OCH_2), 5.06 (q, 1, J = 1.5 Hz, vinyl H), 5.36 (broad s, 1, vinyl H), and 7.2 (m, 4, aryl)). Anal. Calcd for $C_{13}H_{19}O_4P$ (270.29): C, 57.77; H, 7.09. Found (**3**): C, 57.50; H, 7.12. (**4**): C, 57.64; H, 7.17.

The substituted cumyl chlorides were prepared by HCl addition[16] to the 2-arylpropenes and were used directly for kinetic determination after evaporation of solvent: *p*-acetoxycumyl chloride (**5**) (NMR ($CDCl_3$) δ 1.96 (s, 6, 2 Me), 2.24 (s, 3, AcO), and 7.22 (quartet, 4, aryl)); *m*-acetoxycumyl chloride (**6**) (NMR (CCl_4) δ 1.94 (s, 6, 2 Me), 2.20 (s, 3, AcO), and 7.2 (m, 4, aryl)); diethyl *p*-phosphoryloxycumyl chloride (**7**) (NMR ($CDCl_3$) δ 1.33 (t, 6, $J_{H\text{-}H}$ = 7, $J_{P\text{-}H}$ = 1 Hz, 2

Me), 1.89 (s, 6, 2 Me), 4.21 (m, 4, 2 OCH_2), and 7.34 (quartet, 4, aryl)); and diethyl *m*-phosphoryloxycumyl chloride (**8**) (NMR ($CDCl_3$) δ 1.34 (t, 6, $J_{H-H} = 7$, $J_{P-H} = 1$ Hz, 2 Me), 1.96 (s, 6, 2 Me), 4.23 (m, 4, 2 OCH_2), and 7.3 (m, 4, aryl)).

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References and Notes

(1) (a) Undergraduate research participant. (b) National Science Foundation College teacher summer research participant from Winthrop College, Rock Hill, S.C.

(2) (a) E. P. Lyznicki, Jr., and T. T. Tidwell, *J. Am. Chem. Soc.*, **95**, 4935 (1973); (b) R. D. Frampton, T. T. Tidwell, and V. A. Young, *ibid.*, **94**, 1271 (1972).

(3) C. Triantaphylides, G. Peiffer, and R. Gerster, *Bull. Soc. Chim. Fr.*, 1756 (1973).

(4) C. A. Bunton and L. Robinson, *J. Am. Chem. Soc.*, **91**, 6072 (1969).

(5) F. W. Lichtenthaler and F. Cramer, *Chem. Ber.*, **95**, 1971 (1962).

(6) A. Arcoria, S. Fisichella, and F. Sardo, *J. Org. Chem.*, **37**, 2612 (1972).

(7) (a) D. S. Noyce and R. M. Pollack, *J. Am. Chem. Soc.*, **91**, 7158 (1969); (b) D. S. Noyce and R. M. Pollack, *ibid.*, **91**, 119 (1969); K. Yates, *Acc. Chem. Res.*, **4**, 136 (1971).

(8) E. K. Euranto and L. Hautoniemi, *Acta Chem. Scand.*, **23**, 1288 (1969).

(9) (a) K. Oyama and T. T. Tidwell, *J. Am. Chem. Soc.*, **98**, 947 (1976); (b) P. Knittel and T. T. Tidwell, *ibid.*, following paper in this issue; (c) W. K. Chwang, P. Knittel, K. M. Koshy, and T. T. Tidwell, *ibid.*, preceding paper in this issue.

(10) D. G. Garratt, A. Modro, K. Oyama, G. H. Schmid, T. T. Tidwell, and K. Yates, *J. Am. Chem. Soc.*, **96**, 5295 (1974).

(11) (a) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967); (b) T. B. Posner and C. D. Hall, *J. Chem. Soc., Perkin Trans. 2*, 729 (1976). Table 3 in this paper contains printing errors; the constant reported here is that intended (C. D. Hall, private communication); (c) P. B. D. de la Mare, N. S. Isaacs, and M. J. McGlone, *ibid.*, 784 (1976); in unpublished results privately communicated these authors have found values of σ^+ of −0.08 and 0.25 for *p*- and *m*-AcO, respectively. (d) The same NMR method was also reported by A. Cornelis, S. Lambert, and P. Laszlo, *J. Org. Chem.*, **42**, 381 (1977).

(12) R. W. Bott, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 6306 (1965).

(13) (a) F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2299 (1959); (b) C. Eaborn and P. M. Jackson, *J. Chem. Soc. B*, 21 (1969).

(14) C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970.

(15) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(16) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).

(17) H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1897 (1957).

(18) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

(19) (a) H. Gilman et al., *J. Org. Chem.*, **19**, 1067 (1954); (b) B. J. Jandorf, T. Wagner-Jauregg, J. J. O'Neill, and M. A. Stolberg, *J. Am. Chem. Soc.*, **74**, 1521 (1952).

(20) E. C. Leisegang, J. C. Paterson-Jones, and A. M. Stephen, *J. S. Afr. Chem. Inst.*, **23**, 1 (1970); *Chem. Abstr.*, **72**, 133482s (1970).

(21) A. J. Kresge, H. J. Chen, and Y. Chiang, *J. Chem. Soc., Chem. Commun.*, 969 (1972).

(22) E. P. Lyznicki, Jr., K. Oyama, and T. T. Tidwell, *Can. J. Chem.*, **52**, 1066 (1974).

(23) C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).

(24) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 425 (1958).

(25) For references to saturation effects see ref 9a and A. J. Hoefnagel, M. A. Hoefnaegel, and B. M. Wepster, *J. Am. Chem. Soc.*, **98**, 6194 (1976).

(26) E. W. Washburn, Ed. "International Critical Tables", Vol. 3, McGraw-Hill, New York, N.Y., 1928, p 56.

(27) (a) G. Sosnovsky, E. H. Zaret, and A. Gasiecki, *Z. Naturforsch. B*, **30**, 724 (1975); (b) G. Sosnovsky and E. H. Zaret, *Chem. Ind.* (*London*), 1297 (1967).

(28) R. C. DeSelms and T.-W. Lin, *J. Org. Chem.*, **32**, 2023 (1967).

(29) N. D. Field and J. R. Schaefgen, *J. Polym. Sci.*, **58**, 533 (1962).

(30) (a) E. M. Gaydou, *Can. J. Chem.*, **51**, 3412 (1973); (b) E. M. Gaydou and J. R. Llinas, *Org. Magn. Reson.*, **6**, 23 (1974).

(31) J. F. Allen and O. H. Johnson, *J. Am. Chem. Soc.*, **77**, 2871 (1955).

(32) P. A. Levene in "Organic Syntheses", Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N.Y., 1943, p 88.

(33) R. E. Ireland and G. Pfister, *Tetrahedron Lett.*, 2145 (1969).

(34) I. J. Borowitz, S. Firstenberg, E. W. R. Casper, and R. K. Crouch, *J. Org. Chem.*, **36**, 3282 (1971).

(35) E. M. Kosower, W. J. Cole, G.-S. Wu, D. E. Cardy, and G. Meisters, *J. Org. Chem.*, **28**, 630 (1963).

(36) J. F. Arens and T. Doornbos, *Recl. Trav. Chim. Pays-Bas*, **74**, 79 (1955).

(37) J. A. Landgrebe and L. W. Becker, *J. Am. Chem. Soc.*, **90**, 395 (1968).

(38) B. Zwanenburg, *Recl. Trav. Chim. Pays-Bas*, **82**, 593 (1963).

Acid-Catalyzed Hydration of 1,2-Disubstituted Alkenes

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Abstract: *cis*- and *trans*-1,2-dicyclopropylethylene are protonated by aqueous acid at rates 5.6×10^5 and 1.4×10^6, respectively, times slower than their isomer 1,1-dicyclopropylethylene. *cis*- and *trans*-1-cyclopropylpropene are protonated at rates 3.2×10^3 and 7.4×10^3, respectively, times slower than the isomeric 2-cyclopropylpropene. The rate effects show that the position of the proton in the transition state is highly unsymmetrical relative to the double bond, corresponding to the $A_{SE}2$ mechanism of rate-determining proton transfer to carbon. The effect of the substituent on the β carbon undergoing protonation can be accounted for by consideration of the electron-donating ability of the substituent in the transition state and the effect of the substituent on the ground state stability of the olefin. The rates of the 1,2-disubstituted alkenes are quantitatively correlated by the equation $\log k_2 = -12.3[\sigma_p{}^+ + 0.60(\sigma_m{}^+ + 0.08D - 0.084)] - 10.1$ where $\sigma_p{}^+$ and $\sigma_m{}^+$ are the electrophilic substituent constants for the α and β substituents, respectively, and D is the double bond stabilization parameter for the β substituent.

In previous work in this laboratory[1] the rates of acid-catalyzed hydration of 1,1-disubstituted alkenes (eq 1) were found to be correlated with $\sigma_p{}^+$ parameters of the substituents R by eq 2. These results confirmed that these compounds were reacting by the $A_{SE}2$ mechanism with rate-determining protonation on carbon giving a stabilized carbonium ion.

$$R_2C{=}CH_2 \xrightarrow[\text{slow}]{H^+} R_2\overset{+}{C}CH_3 \xrightarrow{H_2O} R_2COHCH_3 \qquad (1)$$

$$\log k_2 = -12.3\Sigma\sigma_p{}^+ - 10.1 \qquad (2)$$

It appeared that the extension of our analysis to hydration of alkenes substituted on both carbons of the double bond would be informative. Previous correlations[1,2] of hydration data have not included such alkenes, and other electrophilic additions for which such treatments have been reported often involve fewer compounds, suffer from mechanistics complications such as bridging, and cover small ranges of reactivity.[2] It would seem particularly worthwhile to develop a consistent picture of the effect of substituents on both the 1 and 2 positions of alkenes in protonations as this is conceptually the simplest