Anal. Calcd for $C_{30}H_{29}O_3P$: C, 76.94; H, 6.20; P, 6.62. Found: C, 76.91; H, 6.31; P, 6.65.

The filtrates from these recrystallizations were evaporated to dryness and the recovered solid was shown to be a mixture of *dl* diols and *dl* acetals by NMR. There were clearly exchangeable protons and at least two different aromatic methyl groups in the NMR spectrum of the solid. Also 11% of the starting **1** was recovered and identified by its ir and NMR spectra.

Reaction of 2a with *p*-Tolualdehyde. An exchange reaction was attempted wherein **2a** (0.88 g, 2 mmol) was heated with an equimolar amount of *p*-tolualdehyde (0.24 g, 2 mmol) in refluxing benzene with one or two crystals of TsOH for 24 hr. After the reaction mixture was cooled for 1 hr, the solid present was collected (0.45 g), washed with ether, and identified as unchanged **2a** by its NMR spectrum (51% recovery). The filtrate was dried in vacuo and the solid which formed was collected by washing with ether (0.26 g, 29.5% yield based on one *p*-tolualdehyde group per acetal). The second solid was shown to contain 30% of the *p*-tolualdehyde moiety by its NMR spectrum. A third crop of solid (0.07 g, 8% yield) was shown to contain about 60% of the *p*-tolualdehyde moiety. These percentages of *p*-tolualdehyde are expressed in terms of one of the benzaldehyde groups being replaced by *p*-tolualdehyde and were arrived at by taking the integration of the aromatic protons signal and dividing by 19 (the number of aromatic protons if there are three phenyl groups and one *p*-tolyl group). The integration of the aromatic methyl region was divided by 3 and the ratio of the integration per hydrogen in the methyl region to that value in the aromatic region was used as the measure of incorporation of the *p*-tolualdehyde group in the acetal. Recrystallization of the latter two solids removed most of **2a** as crystalline compound (0.18 g of 0.30 g). The filtrates were allowed to evaporate to dryness at room temperature and the solid was collected by washing with ether. This solid (0.11 g) contained 75% of one *p*-tolualdehyde group per acetal.

Registry No.—*dl*-**1**, 55145-51-2; **2a**, 36871-89-3; **2s**, 55176-81-3; **13**, 55145-52-3; benzaldehyde, 100-52-7; *p*-tolualdehyde, 104-87-0.

References and Notes

(1) (a) Taken in part from the Ph.D. Dissertation of Armand B. Pepperman, Jr., Louisiana State University in New Orleans, 1973; (b) one of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture; (c) formerly Louisiana State University in New Orleans.
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Steric Effects in the Hydrolysis of Methyl- and *tert*-Butylphenylphosphinic Chloride and Fluoride[1]

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In aqueous acetone methylphenylphosphinic chloride and fluoride are much more reactive than the corresponding *tert*-butylphenylphosphinic halides in solvolysis and reaction with hydroxide ion. With the *tert*-butyl compounds, the fluoride is the more reactive toward hydroxide ion, but the chloride is more reactive in solvolysis, and solvolysis of the fluoride is very slow and autocatalyzed. All the reactions appear to be SN2 (P) displacements and have negative $\Delta S^{\ddagger}$, and steric hindrance by the *tert*-butyl group markedly increases $\Delta H^{\ddagger}$. Solvolysis of methylphenylphosphinic fluoride follows the Grunwald–Winstein equation with $m \sim 0.4$, but plots of log k against Y are curved for *tert*-butylphenylphosphinic chloride, although in the more aqueous solvents the plot is linear with $m \sim 0.6$.

Nucleophilic displacement at a phosphinyl group generally follows an associative, SN2 (P) mechanism, for both solvolysis and reaction in the presence of good nucleophiles, e.g., hydroxide ion.[2] However, it is sometimes possible to use bulky substituents to force a change to a dissociative, SN1 (P) mechanism.[5]

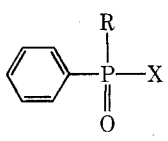
Part of the evidence for this mechanistic change came from markedly different solvent effects upon dissociative and associative reactions, based upon solvent nucleophilicities and the use of the Winstein–Grunwald mY equation. This equation was initially applied to SN reactions at saturated carbon.[6]

Substituent effects upon reaction rates and activation parameters have been rationalized in terms of steric and electronic effects upon nucleophilic attack on phosphorus. Inversion of configuration at phosphorus has been demonstrated,[7] although there is evidence in some reactions for build-up of a pentacovalent intermediate.[8]

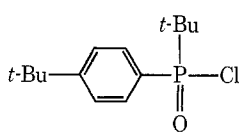
Electrophilic catalysis is often observed, and reactions of esters and fluorides are catalyzed by Brønsted and Lewis acids.[3-5,9a,b]

The aim of the present work was to compare reactions of phosphinyl chlorides and fluorides, because the strength of the P–F bond should make a dissociative mechanism less probable, but strong electron withdrawal by fluoride should assist a reaction in which bond making dominates, and the difference in the importance of bond making and breaking should make the fluorides much more discriminating than the chlorides to nucleophilic attack.

The compounds used were



Ia, X = F
b, X = Cl
R = Me, *t*-Bu



II

so that steric effects were varied, but electronic effects were approximately constant.

We had earlier found that *tert*-butylphenylphosphinic chloride (Ib, R = *t*-Bu) and *tert*-butyl-*p*-*tert*-butylphenylphosphinic chloride (II) were relatively unreactive in hydroxylic solvents,[10] and it seemed possible that these slow reactions might be dissociative. It was necessary to use a range of solvent compositions, in part because some of the substrates are sparingly soluble, and we used aqueous acetone to avoid reaction with the organic component of the solvent.

Experimental Section

Materials. The chlorides were prepared from the phosphinic acids using freshly distilled thionyl chloride,[11] but *tert*-butylphenylphosphinic chloride (Ib, R = *t*-Bu) was also prepared from phenyldichlorophosphine in CH_2Cl_2–$AlCl_3$ and *tert*-butyl chloride. Both samples had identical properties. The preparation of *tert*-butyl-*p*-*tert*-butylphenylphosphinic chloride (II) has been described.[10]

The phosphinic acids were prepared by standard methods. Methyl methylphenylphosphinate was prepared from dimethyl phenylphosphonite and methyl iodide and was saponified (1 *M* NaOH) to give methylphenylphosphinic acid, mp 135.5–136° (lit.[12] mp 136–136.5°). *tert*-Butylphenylphosphinic acid was prepared from phenylphosphonic dichloride and *tert*-butylmagnesium chloride, mp 155–157° (lit.[10,13] mp 154–156°). It proved to be more convenient to make *tert*-butylphenylphosphinic chloride directly.

The fluorides were obtained by heating the chloride under reflux with dried KF in dry MeCN.[14] The reaction was followed by withdrawing samples and examining the ir spectrum, using the bands: for Ia, R = Me, 825 (P–F), 1260 (P=O of the fluoride), 1237 (P=O for the chloride), and 695 cm^{-1} (Ph–P); and for Ia, R = *t*-Bu, ca. 835 (P–F), 1256 (P=O of the fluoride), 1230 (P=O of the chloride), and 634 and 698 cm^{-1} (Ph–P). The fluorides were isolated by vacuum distillation. Methylphenylphosphinic fluoride (Ia, R = Me) had bp 80–82° (0.5 mm) [lit.[14] bp 101–102.5° (4 mm)], and *tert*-butylphenylphosphinic fluoride (Ia, R = *t*-Bu) had mp 40–42°, bp 73° (0.03 mm) in a molecular still. (Anal. Calcd for $C_{10}H_{14}FOP$: C, 60.0; H, 7.0. Found: C, 59.8; H, 6.8.) *p*-*tert*-Butylphenyl-*tert*-butylphosphinic fluoride was prepared in the same way, mp 100–102°. It was unreactive in solvolysis and its reactions were not studied quantitatively.

The NMR and mass spectra of the *tert*-butyl derivatives and their chlorides have been reported.[10] The evidence for structure, based on the NMR spectra, is given below. All the spectra are at 60 MHz (Varian T-60), and except where noted are in $CDCl_3$ and are relative to Me_4Si. The values in parentheses are peak areas. Methyl methylphenylphosphinate: doublet (Me), δ 1.58, 1.80 (3) doublet (OMe), 3.52, 3.74 (3), multiplet 7.6–7.95 (5). Dimethyl phenylphosphonite: doublet (OMe) δ 3.42, 3.60 (6), multiplet 7.3–7.7 (5). Methylphenylphosphinic acid in D_2O with external Me_4Si: doublet (Me), δ 1.60, 1.84 (3.2) (J = 14.4 Hz), multiplet 7.7–8.1 (5). Methylphenylphosphinic chloride: doublet (Me) δ 2.08, 2.33 (3) (J = 15.0 Hz), multiplet 7.4–8.1 (5.2). Methylphenylphosphinic fluoride: doublet of doublets δ 1.68, 1.80 (J = 7.2 Hz, FH) and 1.93, 2.05 (J = 7.2 Hz, FH), and for PH (J = 15 Hz), area 3, multiplet 7.5–8.1 (5.1). *tert*-Butylphenylphosphinic fluoride: doublet of doublets, δ 1.08, 1.10 (J = 1.2 Hz, FH) and 1.37, 1.39 (J = 1.2 Hz, FH), and for PH, J = 17.4 Hz (area 9.3), multiplet 7.42–8.00 (5.0). *tert*-Butyl-*p*-*tert*-butylphenylphosphinic fluoride: doublet (*t*-Bu) δ 1.05, 1.30 (9) (J = 15 Hz), singlet (*t*-Bu) 1.33 (9), multiplet 7.5 (4).

Kinetics. Where possible, reactions of the chlorides were followed conductimetrically. The cells had ground joints which were sealed with Apiezon-W wax to prevent evaporation. This method was not always applicable and several others were also used. Solvolysis of the fluorides was followed using polyethylene or Teflon bottles from which aliquots were removed using a polyethylene pipette, and for most reactions were titrated against NaOH. Reaction of *tert*-butylphenylphosphinic chloride and fluoride with hydroxide ion was also followed by acid–base titration after quenching in cold acetone, and reaction of *tert*-butylphenylphosphinic chloride with hydroxide ion was also followed by potentiometric titration of chloride ion with $AgNO_3$. Reaction of methylphenylphosphinic fluoride with hydroxide ion was followed using a Radiometer pH Stat, with 0.1 *M* KOH as titrant. The reaction of *tert*-butylphenylphosphinic fluoride with hydroxide ion was also followed using an Orion fluoride ion electrode. The pH was brought to 8–9 (HNO_3) and EtOH (20 ml) was added to the 10-ml aliquot. Lanthanum nitrate was used as titrant. We were unable to obtain consistent results with this procedure unless we kept the electrolyte concentration constant, and the equivalence point of the titration depended on the nitrate ion concentration, but this might have been a vagary of the particular electrode which we used.

No single method could be used under all conditions, but the agreement was reasonable where comparisons could be made. In particular the *tert*-butyl derivatives are sparingly soluble in solvents of high water content, and because of the very different reactivities of the substrates we had to use a range of solvents and temperatures, and comparisons then involved large extrapolations, usually using the Arrhenius equation.

The kinetic solvents (aqueous acetone) were made up by weight to correspond to the quoted volume–volume composition. The observed first-order rate constants, k_ψ, are in reciprocal seconds.

Results

Methylphenylphosphinic Fluoride. In water–acetone (90:10 v/v) at 20.0° pK_w = 14.28,[15] and this value was used to calculate the hydroxide ion concentration in the reaction mixture. The values of k_ψ are in Table I, and they fit eq 1

$$k_\psi = k_0 + k_{OH}C_{OH^-} \quad (1)$$

where $k_0 = 3.1 \times 10^{-4}$ sec^{-1} and $k_{OH} = 9.0 \times 10^3$ l. mol^{-1} sec^{-1}.

For reactions in water–acetone (95:5 v/v) we assumed that the small amount of acetone (<1 mol %) would not materially affect K_w, and calculated C_{OH^-} using K_w for water at various temperatures.[16] The values of k_0 and k_{OH} are given in Table II.

Table I
Reaction of Methylphenylphosphinic Fluoride (Ia, R = Me) in Water–Acetone (90:10 v/v)[a]

pH	$10^4 k_\psi$, sec^{-1}	pH	$10^4 k_\psi$, sec^{-1}
5.5	3.00	6.5	4.45
6.0	4.27	7.0	8.27
6.25	4.30	7.5	17.7

[a] At 20.0° and 2×10^{-3} *M* substrate.

Table II
Rate Constants for Reactions of Methylphenylphosphinic Fluoride in Water–Acetone (95:5 v/v)

Temp, °C	$10^4 k_0$, sec^{-1}	$10^{-3} k_{OH}$, l. mol^{-1} sec^{-1}
0.0	1.49	2.73
10.0	2.50	4.44
15.0	3.22	5.50
20.0	4.3[a]	6.8[a]
25.0	5.50	8.43

[a] Interpolated using the Arrhenius equation.

The values of k_0 obtained over a range of solvents and temperatures, and usually by acid–base titration, are given in Table III.

Table III
Solvolysis of Methylphenylphosphinic Fluoride[a]

	% H_2O (v/v)						
Temp, °C	20	30	40	50	70	90	95
20.0						3.10	4.3
25.0	0.40	0.99	1.50	2.93			5.50
35.0		1.65		4.78	8.63		
50.0		3.84		10.4			

[a] Values of $10^4 k$

***tert*-Butylphenylphosphinic Chloride.** Solvolysis of this chloride is relatively slow and could be followed conductimetrically over a range of temperatures and aqueous acetone solvents (Table IV). The reaction with hydroxide ion was followed by acid–base titration or by potentiometric titration of chloride ion (Table V). A plot of k_ψ against hydroxide ion concentration in water–acetone (90:10 v/v) at 20.0° is slightly curved, presumably because of a salt effect at high hydroxide ion concentration, and the second-order rate constant, $k_{OH} = 2.8 \times 10^{-4}$ l. mol^{-1} sec^{-1}, is calculated from the initial slope of the plot.

Table IV
Solvolysis of *tert*-Butylphenylphosphinic Chloride (Ib, R = *t*-Bu) in Aqueous Acetone[a]

	% H_2O (v/v)			
Temp, °C	50	70	90	95
35.0	0.047	0.119	0.333	0.424
50.0	0.163	0.420	1.20	1.55
60.0	0.340	0.901	2.46	3.23

[a] Values of $10^4 k_\psi$, sec^{-1}.

Table V
Reaction of *tert*-Butylphenylphosphinic Chloride with Hydroxide Ion[a]

c_{OH^-}, *M*	$10^5 k_\psi$, sec^{-1}	c_{OH^-}, *M*	$10^5 k_\psi$, sec^{-1}
	0.87[b]	0.1	0.67[e]
	0.11[c]	0.3	11.9
0.01	1.28[d]	0.5	20.7
0.1	3.13		

[a] In water–acetone (90:10 v/v) at 20.0° with KOH followed by titration of chloride ion unless specified. [b] Extrapolated from results in Table IV. [c] Extrapolated to 0°. [d] Acid–base titration. [e] At 0°.

***tert*-Butyl-*p*-*tert*butylphenylphosphinic Chloride.** Solvolysis of this chloride was followed conductimetrically (Table VI) in order to estimate the effect of a *tert*-butyl group in the para position. Comparison of the results in Tables IV and VI show that the rate of solvolysis is halved by the para substituent.

Table VI
Solvolysis of *tert*-Butyl-*p*-*tert*-butylphenylphosphinic Chloride (II)[a]

	% H_2O (v/v)					
Temp, °C	30	40	50	70	90	95
25.0					0.058	0.083
35.0			0.022	0.054	0.161	0.204
50.0	0.027	0.047	0.070	0.182	0.620	0.829
60.0			0.171	0.478		

[a] Values of $10^4 k_\psi$, sec^{-1}.

***tert*-Butylphenylphosphinic Fluoride.** In the presence of hydroxide ion, plots of k_ψ against hydroxide ion (Table VII) are linear with very small intercepts. The values of $10^3 k_{OH}$ are ca. 1.5 l. mol^{-1} sec^{-1} at 0° and 7.44 l. mol^{-1} sec^{-1} at 20.0° in water–acetone (90:10 v/v).

Solvolysis is very slow and was followed by acid–base titration, but with substrate concentrations sufficient for analysis the product precipitated during the run. These solvolyses gave curved first-order plots and the values of k_ψ given in Table VIII are calculated from the initial slopes of the plots and are less accurate than the other rate constants. The curvature may be due to autocatalysis rather than to product precipitation because 0.05 *M* perchloric acid strongly catalyzes the reaction, and at 60.0° $10^5 k_\psi$ = 1.3 sec^{-1} in water–acetone (40:60 v/v) and 2.5 sec^{-1} in water–acetone (80:20 v/v). (In the absence of strong acid the solvolysis is too slow to be followed in 40% water.)

Table VII
Reaction of *tert*-Butylphenylphosphinic Fluoride with Hydroxide Ion in Water–Acetone (90:10 v/v)[a]

	c_{OH^-}, *M*		
Temp, °C	0.01	0.02	0.025
0.0		3.00	3.72
20.0	8.42	14.7	19.7, 17.9[b]

[a] Values of $10^5 k_\psi$, sec^{-1}, determined by acid–base titration except where specified. [b] Followed by potentiometric titration of fluoride ion.

Table VIII
Solvolysis of *tert*-Butylphenylphosphinic Fluoride[a]

	% H_2O (v/v)	
Temp, °C	80	90
60.0	2.3	6.0

[a] Values of $10^7 k_\psi$, sec^{-1}, followed by acid–base titration.

Solvent Effects upon Solvolytic Reactions. Solvent effects often depend on mechanism, and we therefore compared the solvent effects upon the solvolyses of some of these phosphinic halides using the Winstein–Grunwald equation.[6] There is no a priori reason why this equation should apply accurately to these solvolyses, but the *Y* solvent parameter gives a good indication of the ionizing power of a solvent and has been applied to other solvolyses of phosphorus compounds.[5]

The relations between log k_ψ and *Y* are shown in Figure 1 for solvolysis of methylphenylphosphinic fluoride at 25°, of *tert*-butyl-*p*-*tert*-butylphenylphosphinic chloride at 50°, and of *tert*-butylphenylphosphinic chloride over a temperature range. The plot is linear only for solvolysis of

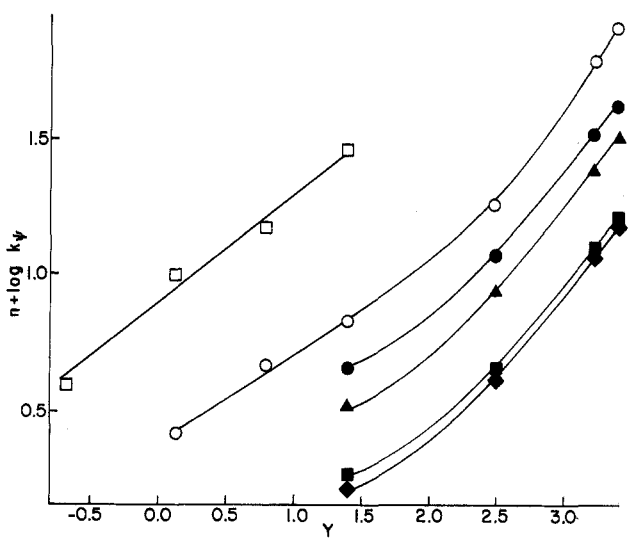


Figure 1. Solvent effects upon solvolysis: □, methylphenylphosphinic fluoride at 25.0°, n = 5; ○, *tert*-butyl-*p*-*tert*-butylphenylphosphinic chloride at 50.0°, n = 6. Solid points (*tert*-butylphenylphosphinic chloride): ■, at 25.0°, n = 6; ● at 35.0°, n = 6; ♦, at 50.0°, n = 5; ▲, at 60.0°, n = 5.

Table IX
***m* Values for Solvolyses**

Substrate	Temp, °C	*m*
t-BuP(Ph)OCl	25	0.62
	35	0.60
	50	0.60
	60	0.62
p-*t*-BuPhP(*t*-Bu)OCl	50	0.66 (0.34[a])
MeP(Ph)OF	25	0.36

[a] From the slope at lower *Y* values.

methylphenylphosphinic fluoride. However, the slopes of the plots are insensitive to temperature changes. The plots are approximately linear for solvolyses of the chlorides in the more aqueous solvents, and the values of *m* given in Table IX are calculated from these linear portions; for the *p*-*tert*-butyl compound (II) the value of *m* given in parentheses is the approximate slope for the region 20–40% water.

The solvolysis of methylphenylphosphinic chloride is too fast, and that of *tert*-butylphenylphosphinic fluoride is too slow, for estimation of solvent effects on rate.

For similar substrates a solvolytic dissociative mechanism would be expected to have a higher *m* value than a bimolecular reaction with lyate ion,[6] but it is difficult to make a prediction of the probable *m* value for attack by solvent upon a phosphinyl group. The use of solvents of similar *Y* values but different nucleophilicities suggested that *m* values tended to be lower (ca. 0.2) for bimolecular solvent attack upon phosphorus than for a dissociative mechanism ($m \sim 0.5$),[5a] but the range of *m* values was small. Our values tend toward those considered to be characteristic of dissociative mechanisms (Table IX), but all our other evidence supports an associative SN2 (P) mechanism, and because some of our *mY* plots are curved we feel that this rate–solvent relationship is not a good mechanistic test for solvolysis of these phosphinic halides.

Activation Parameters for Solvolysis. The activation parameters given in Table X are not markedly dependent upon solvent composition, but the large differences between the solvents used in our work and the relatively nonaqueous solvent used for the solvolysis of methylphenylphosphinic chloride[17] complicate comparisons. Some of the parameters were determined over small temperature ranges, and their values are therefore not accurate.

Table X
Activation Parameters for Solvolysis

Substrate	% H_2O	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
MeP(Ph)OCl[a]	5	6.0	−26
MeP(Ph)OF	30	9.7	−44
	50	9.2	−44
	95	7.9	−47
t-BuP(Ph)OCl	50	16	−32
	70	16	−30
	90	16	−28
	95	16	−27
p-*t*-BuPhP(*t*-Bu)OCl	50	16	−33
	70	17	−27
	90	17	−24
	95	17	−25

[a] Reference 17.

For solvolysis of the *tert*-butylphenylphosphinic chlorides the kinetic solvent effect is largely on $\Delta S^{\ddagger}$, which becomes more negative as the solvent becomes drier (Table X), but for solvolysis of methylphenylphosphinic fluoride it is $\Delta H^{\ddagger}$ which increases as the solvent becomes drier with $\Delta S^{\ddagger}$ becoming slightly less negative. These differences could be related to hydrogen bonding between water and a departing fluoride ion, which should lower $\Delta H^{\ddagger}$. Unfortunately, we could not obtain activation parameters for the other substrates to test this hypothesis. The *tert*-butylphosphinic chlorides have much higher activation enthalpies than the methyl compounds, because of the steric bulk of the *tert*-butyl group.

Comparison of Reactivities toward Hydroxide Ion. The *tert*-butyl group considerably hinders nucleophilic attack, so that the reactions with hydroxide ion had to be followed at different temperatures, and where necessary extrapolations were made using the Arrhenius equation. The second-order rate constants are summarized in Table XI, and the activation parameters are in Table XII. These parameters are in the range expected for SN2 (P) reactions, and steric hindrance by the *tert*-butyl group shows up in both the enthalpy and entropy terms, as for solvolysis (Table X).

Table XI
Reactions with Hydroxide Ion[a]

Substrate	Temp, °C	k_{OH}, l. mol^{-1} sec^{-1}
MeP(Ph)OF	20.0	9030
	0.0	2730[b]
	10.0	4440[b]
	15.0	5500[b]
	20.0	6800[b]
	25.0	8430[b]
t-BuP(Ph)OF	0.0	1.5×10^{-3}
	20.0	7.4×10^{-3}
t-BuP(Ph)OCl	0.0	5.6×10^{-5}
	20.0	2.8×10^{-4}

[a] In water–acetone (90:10 v/v) except where specified. [b] In water–acetone (95:5 v/v).

Table XII
Activation Parameters for Reaction with Hydroxide Ion

Substrate	% H_2O (v/v)	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
MeP(Ph)OF	95	6.7	−18
t-BuP(Ph)OF	90	12	−34
t-BuP(Ph)OCl	90	12	−40

Activation enthalpies for attack of hydroxide ion upon fluorophosphonates, dialkylfluorophosphates, and diethylphosphonic fluoride and the corresponding unhindered chlorides are generally in the range 6–12 kcal mol^{-1}, and the activation entropies are negative, and in the range −15 to −35 eu. This pattern is typical of the attack of hydroxide ion on phosphorus.[3,4,17–19]

Although acid chlorides are generally more reactive than fluorides in solvolysis, the opposite is often found for reaction with hydroxide ion because the stronger electron withdrawal by a fluoride substituent overcomes the easier loss of chloride.[20] This pattern is observed with the *tert*-butylphenylphosphinic halides (Table XI).

The *tert*-butyl group has a very large effect on the attack of hydroxide ion and in water–acetone (90:10 v/v) methylphenylphosphinic fluoride (Ia, R = Me) is more reactive than the *tert*-butyl compound (Ia, R = *t*-Bu) by a factor of approximately 10^6 (Table XI). We could not make a rate

comparison for the chlorides because of the very high reactivity of methylphenylphosphinic chloride.[17]

Solvolytic Reactions. Our hope of comparing directly the reactivities of the methyl and *tert*-butyl compounds (Ia,b, II) under solvolytic conditions was frustrated by the very low reactivity of *tert*-butylphenylphosphinic fluoride in the absence of hydroxide ion and the very high reactivity of methylphenylphosphinic chloride,[17] and indirect comparisons involve large extrapolations over a range of solvent composition or temperature.

The hydrolysis of many acid fluorides is acid catalyzed because of the basicity of fluoride,[9] and autocatalysis is often observed, for example with dialkyl fluorophosphates and phosphonates[9a] but not with methylphenylphosphinic fluoride, probably because of the smaller dissociation constant of a phosphinic as compared with a phosphonic acid. The hydrolysis of *tert*-butylphenylphosphinic fluoride was autocatalyzed. suggesting that the spontaneous hydrolysis is more subject to steric hindrance by the *tert*-butyl group than the acid hydrolysis, because we found no autocatalysis with the methyl compound. However, conditions were not directly comparable because reaction of the *tert*-butyl compound was followed using a substrate concentration of ca. 10^{-2} *M* as compared with that of ca. 10^{-3} for the methyl compound.

The solvolytic reactivities of *tert*-butylphenylphosphinic chloride and fluoride can be compared directly at 60° in water–acetone (90:10 v/v) (Tables IV and VIII) where the chloride is more reactive than the fluoride by a factor of 410. This difference between the solvolytic reactivities of chlorides and fluorides is general, for example with benzenesulfonyl halides.[20]

Comparison of the solvolytic reactivities of methylphenylphosphinic chloride and fluoride requires considerable extrapolation. The first-order rate constant for the hydrolysis of methylphenylphosphinic chloride at 25° in water–acetone (95:5 v/v) is 0.18 sec^{-1}, calculated using the Arrhenius parameters given in ref 17. Extrapolation of the rate constants of solvolysis of the fluoride (Table III) using the Grunwald–Winstein equation[6] gives the corresponding value of 5.6×10^{-6} sec^{-1}. [Solvolysis of methylphenylphosphinic fluoride gives a linear plot of log *k* against *Y* (Figure 1).] Thus in this solvent of low water content the reactivity difference between methylphenylphosphinic chloride and fluoride is 3×10^4. This reactivity difference is much greater than for the *tert*-butyl compounds, but the difference could be related to differences in solvent and temperature rather than structure.

The *tert*-butyl compounds are much less reactive than the corresponding methyl compounds in solvolysis, and again because of problems due to high reactivity of some compounds and the low solubility of others, we cannot make all the rate comparisons for the methyl and *tert*-butyl compounds under the same conditions. For the chlorides we have to use a solvent of low water content, because of the very high reactivity of methylphenylphosphinic chloride. A very approximate estimate of the relative reactivities can be made on the following basis. In 5% water at 35° the extrapolated rate constant for solvolysis of methylphenylphosphinic chloride[17] is 0.26 sec^{-1}, and in 50% water at 35° $k_0 = 4.7 \times 10^{-6}$ sec^{-1} for the *tert*-butylphenylphosphinic chloride (Table IV). Although log *k* vs. *Y* plots are curved for solvents of low water content (Figure 1), $m \sim 0.3$ in these solvents, giving an approximate extrapolated value of $k_0 \simeq 2 \times 10^{-7}$ sec^{-1} at 35° in 5% water, so that the methyl would be more reactive than the *tert*-butyl compound by a factor of approximately 10^6 under these conditions.

Comparison of the reactivities of the fluorides has to be made using an aqueous solvent and a relatively high temperature. From the solvent and temperature effects upon the solvolysis of methylphenylphosphinic fluoride (Table III) we estimate $k_0 \simeq 1.7 \times 10^{-3}$ sec^{-1} at 60° in water–acetone (90:10 v/v), and under these conditions $k_0 = 6 \times 10^{-7}$ sec^{-1} for the *tert*-butyl compound (Table VIII), giving a reactivity difference of 3×10^3. This large difference in the relative effects of methyl and *tert*-butyl groups on hydrolyses of the fluoride and chloride may not be mechanistically significant, in part because different solvent compositions were used, but also because reactions of the *tert*-butyl compounds have higher activation energies than those of the methyl compounds (Table X), so that increasing temperature will reduce the reactivity difference.

Although a *tert*-butyl group sterically deactivates *tert*-butylphenylphosphinic chloride and fluoride strongly, the chloride ($k_0 = 3 \times 10^{-4}$ sec^{-1} at 60° in 95% water) is very much more reactive than di-*tert*-butylphosphinic chloride ($k_0 = 9 \times 10^{-7}$ sec^{-1} at 100° in water). The di-*tert*-butyl compound is believed to react by a dissociative SN1 (P) mechanism,[5a] suggesting that *tert*-butylphenylphosphinic chloride does not react by a dissociative mechanism.

Selectivities of Fluorides and Chlorides toward Nucleophiles. Although all the compounds which we examined appear to react by SN2 (P) mechanisms, a sterically hindered fluoride (Ia, R = *t*-Bu) discriminates very strikingly in favor of reaction with a strong nucleophile, OH^-, as compared with a weak one, H_2O, and this type of selectivity is important in the biological activity of fluorophosphorus compounds. This behavior of fluorides as compared with chlorides toward good nucleophiles appears to be general,[20,21] and can be viewed in terms of Pearson's distinction between hard and soft reagents.[22] This "hardness" of a fluoride as compared with a chloride is also evident in the differences in the P=O stretching frequencies of the phosphorus halides.[14,23] The relative importance of bond making and breaking is also important in that the latter should be easier with a chloride than a fluoride.

Registry No.—Ia (R = Me), 657-37-4; Ia (R = *t*-Bu), 55236-56-1; Ib (R = Me), 5761-97-7; Ib (R = *t*-Bu), 4923-85-7; II, 25097-44-3; *tert*-butyl-*p*-*tert*-butylphenylphosphinic fluoride, 55236-57-2; phenyldichlorophosphine, 644-97-3; *tert*-butyl chloride, 507-20-0; methyl methylphenylphosphinate, 6389-79-3; dimethyl phenylphosphonite, 2946-61-4; methylphenylphosphinic acid, 4271-13-0.

References and Notes

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Regiochemistry and Stereochemistry in the Hydralumination of Heterosubstituted Acetylenes. Interplay of Inductive and Resonance Effects in Electron-Rich Alkynes[1]

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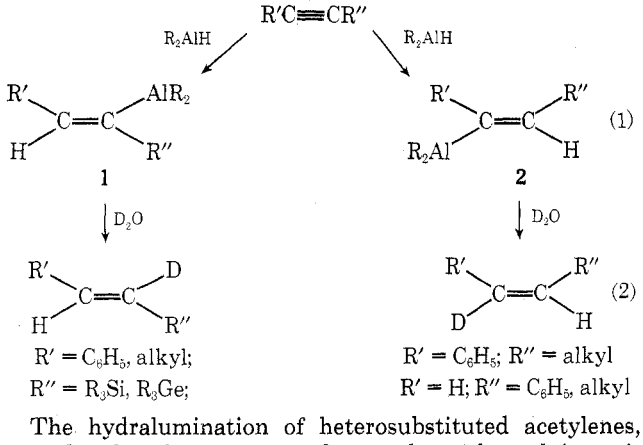
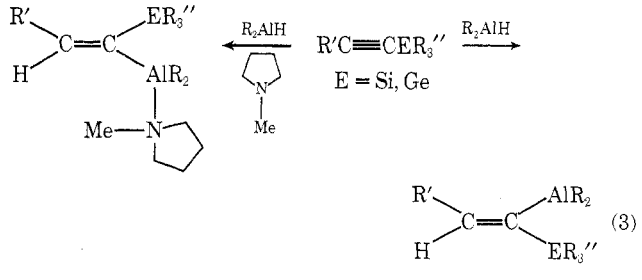
The hydralumination of certain electron-rich alkynes with diisobutylaluminum hydride was studied, in order to determine the influence of inductive and resonance factors on the regiochemistry and stereochemistry of the addition. Dimethyl(phenylethynyl)amine underwent an overall trans hydralumination, which placed the R_2Al group α to the phenyl group. In addition, one-third of the amine was consumed in a competing reductive dimerization. In additions moderated by *N*-methylpyrrolidine, no reductive dimerization of the alkyne was observed, but the initial cis adduct was detected by NMR spectroscopy. Ethyl phenylethynyl sulfide gave only the cis hydralumination adduct with the R_2Al attached to the phenyl-substituted vinyl carbon and the thio-substituted vinyl carbon in a 17:83 ratio. 1-Ethoxy-1-hexyne gave principally the cis hydralumination adduct with the R_2Al group exclusively α to the butyl group. In contrast, both phenylethynyllithium and diphenyl(phenylethynyl)aluminum underwent mono- and bishydraluminations to yield adducts having all metallo groups β to the phenyl group. Finally, chloro- and bromo(phenyl)acetylenes were relatively unreactive toward R_2AlH; at higher temperatures, addition did occur but with concurrent loss of halogen. The foregoing observations are interpreted in terms of a mechanism involving (a) electrophilic attack by R_2AlH on the triple bond; (b) addition of the Al–H bond, in accord with developing p_π–p_π or p_π–d_π polarizations, to yield the cis adduct; (c) isomerization to the trans adduct, where feasible; and (d) for those cases where the corresponding 1-alkyne is also formed, the cis elimination of R_2AlE (where E = Br, Cl, SEt, or OEt) from this trans adduct.

The addition of alkylaluminum hydrides to alkynes, with subsequent hydrolysis, constitutes a mild, convenient method for the cis reduction[2,3] or, in certain cases, the trans reduction[4] of the C≡C group (eq 1). Since the position of the alkylalumino group on the resulting C=C linkage is readily labeled by treatment with D_2O, both the stereochemistry and the regiochemistry of hydralumination can be determined by NMR spectroscopy (eq 2).[3-6]



The hydralumination of heterosubstituted acetylenes, considered in the present study, was deemed worth investigating on several counts. First of all, the interplay of inductive and resonance effects for the heterosubstituent E in R'C≡CE (where E = R_2N, RO, RS, X, or M) could give rise to varying proportions of the four possible aluminum products, adducts **1** and **2** in eq 1 and their two regioisomers. Thus, analysis of these product ratios in terms of electronic effects for group E promised further insight into the nature of the transition state. Secondly, the hydralumination of acetylenic ethers and amines seemed to be a feasible synthetic route to vinylic ethers and enamines, respectively, of defined stereochemistry. Since such hydraluminations occur at or below room temperature and the hydrolytic work-up ensues under mildly basic conditions, these hydrolysis-sensitive olefins were expected to remain intact.

Finally, it was of interest to learn whether the cis or trans stereochemistry of such additions might be subject to kinetic or thermodynamic control. As with the cases of trialkylsilyl- and trialkylgermylacetylenes[5,6] (eq 3), the prospect of achieving cleanly either a cis or a trans hydralumination of these heterosubstituted acetylenes was most attractive.



Results

As model systems, the following available electron-rich acetylenes were subjected to the action of diisobutylaluminum hydride (**3**): dimethyl(phenylethynyl)amine (**4**); 1-eth-