Alkylations Using Methyltrialkoxyphosphonium Tetrafluoborate Salts. Synthetic and Mechanistic Aspects of Methyl, Ethyl, 2-Propyl, and 2-Octyl Group Transfers[1]

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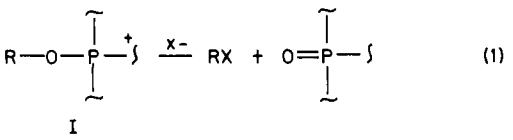
Received June 26, 1984

Trialkyl phosphites, $(RO)_3P$ for R = methyl, ethyl, 2-propyl, and 2-octyl, were alkylated with Meerwein's salt ($Me_3O^+BF_4^-$) to yield the corresponding trialkoxymethylphosphonium tetrafluoborate salts. These salts, which are all molten at room temperature, were reacted neat or in solvents with a series of nucleophiles. Thus, a variety of O, N, S, and halogen nucleophiles reacted by substitution at the R group C–O bond to give high yields after a trivial workup procedure. Rates of reaction were measured for substituted benzoic acids ($4\text{-}XC_6H_4CO_2H$; X = CH_3, *t*-Bu, CH_3O, H, CF_3, CN, NO_2) with the neat salts under pseudo-first-order conditions or with the salt in CH_3CN under second-order conditions. The resulting Hammett plots indicate very little change in sensitivity to the substituents when R = isopropyl compared with R = methyl and when the salt itself instead of CH_3CN is solvent.

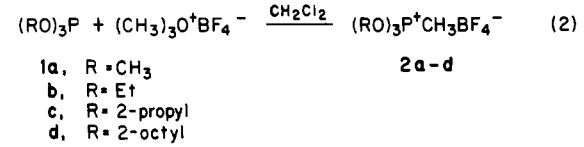
Oxyphosphonium salts are a class of compounds that are excellent incipient alkyl transfer reagents. Cleavage of the alkoxy C–O bond proceeds to generate the highly thermodynamically stable P=O species and provides the driving force (eq 1). The oxyphosphonium species I is



(1)

I

apparently generated as a short-lived intermediate in the Arbusov reaction, where an alkyl iodide is used to alkylate the phosphite and gives the salt I which immediately reacts with iodide at R.[2-4] In the absence of a nucleophile X, one expects these salts to be isolable.[4,5] Thus, methylation of the phosphite **1** with trimethyloxonium tetrafluoborate (TMOT) in CH_2Cl_2 at room temperature yields colorless, slightly viscous oils after reaction and solvent removal[5] (eq 2).



(2)

1a, R = CH_3
b, R = Et
c, R = 2-propyl
d, R = 2-octyl

2a–d

Results and Discussion

Synthetic Results. The results of reactions of these salts **2** with various nucleophiles are given in Table I. Each entry is the average of at least three identical experiments, although no attempt was made to optimize the conditions. No apparent dimunition of yield or ease of workup was observed when scaled-up versions were conducted. However, the exothermicity of very large scale reactions could best be controlled by solvent reflux, and this is simply accomplished by leaving the CH_2Cl_2 solvent from the salt preparation. No extreme precautions were observed to exclude water. Glassware was simply oven-

Table I. Alkylation of Nucleophiles with Oxyphosphonium Salts 2a–d[a]

nucleophile	P^+ salts	yield,[b] %	product(s)[c]	R
$CH_3(CH_2)_6CH_2OH$ (4)	**2a**	99	$CH_3(CH_2)_6CH_2OR$ (5)	CH_3
4	**2c**	99	5	2-propyl
CH_3OH (6)	**2a**	99[d]	CH_3OR (7)	CH_3
6	**2b**	99[d]	7	Et
6	**2c**	>90[d]	7	2-propyl
6	**2d**	71[e]	7[e]	2-octyl
C_6H_5SH (8)	**2a**	72[f]	C_6H_5SR (9)	CH_3
8	**2c**	78[f]	9	2-propyl
$C_6H_5CO_2H$ (10)	**2a**	95[d,g]	$C_6H_5CO_2R$ (11)	CH_3
10	**2c**	90[d,g]	11	2-propyl
$C_6H_5CO_2^-Na^+$ (12)	**2a**	>95[g]	11	CH_3
12	**2c**	>95[g]	11	2-propyl
$(CH_3)_2CHCH_2CO_2H$ (13)	**2a**	95	$(CH_3)_2CH_2CH_2CO_2R$ (14)	CH_3
13	**2c**	90	14	2-propyl
$(CH_3)_2CHCH_2CO_2^-Na^+$ (15)	**2a**	99	14	CH_3
15	**2c**	99	14	2-propyl
cyclohexyl-NH_2 (16)[h]	**2a**	75	*i*	CH_3
16[h]	**2c**	85	*i*	2-propyl
$(CH_3CH_2CH_2)_2NH$ (17)[h]	**2a**	51	*i*	CH_3
17[h]	**2c**	84	*i*	2-propyl

[a] Nucleophile (1.0 mmol) added to a 10% excess of neat salt, stirred at 25 °C for 12 h, quenched by addition of 1 mL of CH_3OH, and analyzed. [b] Gas chromatographic yield measured relative to an internal hydrocarbon standard. Average of at least three replicate runs. Standard deviations are 3–5%. [c] Corresponding phosphonate **3** observed in each case. Yields not determined. [d] Reaction conducted in sealed NMR tube. Product structure determined only from ^1H NMR data. Yield determined relative to phosphonate **3** P–CH_3 intensity by integration. [e] A 29% yield of octenes were obtained. The mixture was not separated but derivatives were made by using Br_2 in CH_3OH to identify the alkene functional group. [f] Starting nucleophile was also isolated. [g] IR data from benzoic acid and its derivatives in Table II indicates an extremely high level of conversion to the esters. Yield limits are set by the detection limit for the acid. [h] Two equivalents amine per equivalent salt **2**. [i] One equivalent of amine is the acid scavenger; product determined after neutralization as a mixture of mono- and dialkylation (~3:1 ratio). Tetraalkylammonium salt was not analyzed for. Yields based on limiting reagent **7**.

(1) Presented in part at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 21, 1983; "Arbusov Reactions in Molten Salts", ORGN 27.

(2) Arbusov, A. E. *J. Russ. Phys. Chem. Soc.* **1906**, *38*, 687; *Chem. Zentr.* **1906**, *II*, 1639.

(3) For a recent review of the Arbusov reaction, see: Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415–30.

(4) For considerable information on formation of alkoxyphosphonium salts and the kinetics and mechanisms of Arbusov reactions, see: (a) Lewis, E. S.; Hamp, D. *J. Org. Chem.* **1983**, *48*, 2025–9. (b) Lewis, E. S.; Colle, K. S. *Ibid.* **1981**, *46*, 4369–72; (c) **1978**, *43*, 571–4.

(5) Compounds similar to **2** were previously prepared and reacted with water and ethanol: Nesterov, L.; Kessel, A.; Maklakov, L. *J. Gen. Chem. USSR* **1968**, *38*, 318.

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dried. Solvents and liquid reagents were distilled and/or stored over molecular sieves. Solids were sublimed and/or dried in a vacuum oven. Indeed, one might expect that small scale reactions (such as those in Table I) have reduced yields due to unavoidable contamination with traces of water.

The reactions of **2** produce a stoichiometric amount of the corresponding phosphonates **3a–d** (eq 3) and acid when

$$2 \xrightarrow{HX} RX + (RO)_2P(=O)CH_3 + H^+ \qquad (3)$$

3a-d

the substrate to be alkylated is in its conjugate acid form (alcohols or carboxylic acids instead of alkoxide or carboxylates, for example). Control runs indicate that reaction of the various nucleophiles with **3** (presumably by substitution at phosphorus) were generally 2 orders of magnitude slower than alkylations with **2**. Thus, virtually no competitive consumption of starting material was observed. In the simple systems examined, the acid generated did not interfere with the reactions in the time scales utilized. For example, sodium benzoate, although it reacts faster, gave no better yield results than benzoic acid itself. Problems arising from interference from the protons generated can be further reduced by working the reaction up after 15 to 30 min. The course of evolution of heat from these reactions implies that they are very rapid and often near instantaneous after mixing. We chose to conduct them all for longer times to assure completion and allow comparison under the same set of conditions. An alternative set of conditions has been explored to assure scavenging of the acid without introduction of a base or nucleophile which might encourage an elimination or an additional substitution reaction. Proton Sponge (1,8-bis(dimethylamino)naphthalene) and 2,6-lutidine are satisfactory in this regard.

Methylation with **2a** appears to be a high and often quantitative yield alternative for alkylation of alcohols, thiols, acids, and carboxylate ions. Ethylation and alkyl transfer from other primary alkoxyphosphonium salts have not been as extensively studied but are equally promising.[11] The salts **2c** and **2d**, which involve secondary carbons at the point of substitution, suffer from diminished yields because of competing elimination reactions. However, substitution is sufficiently dominant to warrant their use synthetically. Salt **2d** was made specifically to enable easy observation of elimination products. It gives larger amounts of alkenes than **2c** apparently because the transition state leading to the more highly substituted 2-octenes is more accessible. Alkylation at nitrogen is complicated by its basicity, a problem overcome by the use of appropriate nonnucleophilic acid scavengers. Nonetheless, the total amount of alkylation is quite substantial especially in the case of **2c** where the amine basicity might be expected to enhance elimination. Reactions with halides, quite efficient in themselves, are no better than the authentic Arbusov reactions or any number of other excellent alternatives.

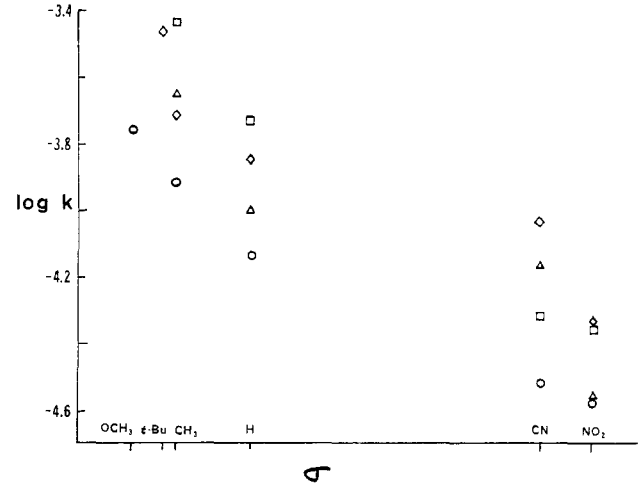

Figure 1. Plot of log k vs. σ for reactions of salt **2** with para-substituted benzoic acids. The solvent was either CH_3CN (R = CH_3 (△) or R = 2-propyl (□)) or the neat salt itself (R = CH_3 (○) or R = 2-propyl (□)).

Table II. Rate Constants for Reaction of 4-$XC_6H_4CO_2H$ with 2a and 2c

		rate constants[a]			
		neat salt 2 10^5k_1, M^{-1} s^{-1}		CH_3CN solvent 10^5k_2, M^{-1} s^{-1}	
X	σ[b]	**2a**	**2c**	**2a**	**2c**
NO_2	0.78	2.6	4.4	2.7	4.5
CN	0.66	3.0	4.8	6.8	9.1
H	0.0	7.2	18.0	10	14
CH_3	−0.17	12	36.0	22	19
t-Bu	−0.20				34
CH_3O	−0.27	18			

[a] Measured from the appearance of the ester carbonyl stretch as described in the Experimental Section; k_1 and k_2 are pseudo-first-order and second-order rate constants, respectively, and are described in eq 4 and 5. The pseudo-first-order rate constants above represent k_1 and not $[2]k_1$. Standard deviations on the rates are 10–15%. [b] Reference 7, p 28.

Kinetic Measurements with Substituted Benzoic Acids. Rates of reaction of **2a** and **2c** with various substituted benzoic acids are presented in Table II. The reactions were conducted in two different ways: (a) by using neat salt **2** as the combination solvent/alkylating reagent under pseudo-first-order conditions ([nucleophile] = 3%[salt **2**]) (eq 4); (b) by using equimolar amounts of

$$\text{rate} = k_1[\text{nucleophile}][\text{salt } 2] \qquad (4)$$

$$\text{where [salt 2] = constant}$$

nucleophile and salt in acetonitrile as solvent under second-order conditions (eq 5). Various techniques were

$$\text{rate} = k_2[\text{nucleophile}][\text{salt } 2] \qquad (5)$$

attempted to measure the course of the reaction in aliquots, including (a) liquid chromatographic separation on a reversed phase C_{18} silica column using a 254-nm absorption detector; (b) gas chromatography of samples quenched with methanol or ethanol; (c) proton NMR integration of ester groups; and (d) infrared detection of the increase of the ester carbonyl intensity. The most successful were the first and the last, and the data in Table II are from d. Data handling capability allowed measuring absorbances of the ester $\gamma_{C=O}$ uncorrected or after subtraction of the nearby acid carbonyl contribution. The

(6) Ford, W. T.; Hauri, R. J.; Smith, S. G. *J. Am. Chem. Soc.* **1974**, *96*, 4316.
(7) "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1972; pp 203–320.
(8) Lowrey, T. H.; Richardson, K. S.; "Mechanism and Theory in Organic Chemistry", 2nd ed., Harper and Row: New York, 1981; pp 130–44.
(9) Meerwein, H. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, pp 1096–8.
(10) Ford-Moore, A. H.; Perry, B. J. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, pp 955–7.
(11) S. E. Fry, unpublished results.

slightly better corrected values were converted to absolute concentrations using calibration curves.

The data in Table II are plotted in a Hammett plot in Figure 1 as log k vs. σ. If one assumes that the data represent straight lines, least-squares fits give the following slopes (R, solvent, ρ): CH_3, salt, −0.74; isopropyl, salt, −0.94; CH_3, CH_3CN, −0.72; isopropyl, CH_3CN, −0.65. All are negative ρ values less than one. Although the differences are rather small and the experimental uncertainty is high (10–15% in Table II), a number of conclusions appear reasonable. The neat salts **2** behave similar to the dipolar aprotic solvent CH_3CN since the absolute values and sensitivity to σ are similar. Parallel results were obtained by Ford[6] during substitution reactions using halide ions with methyl tosylate in dimethylformamide or the organic molten salts, tetraalkylammonium tetraalkylborides. Here again the rates were slightly smaller in the fused salt solvent. No change in slope is observed in CH_3CN and only a very modest increase in fused salt when isopropyl transfer is compared to the methyl transfer. This would indicate an identical or, at least very similar transition state, most likely S_N2. However, the absolute rate constants are a factor of 2–3 higher for **2c** than for **2a**, an observation inconsistent with the greater extent of steric congestion to be expected at the secondary carbon. Additional evidence supporting the S_N2 mechanism includes the high substitution to elimination ratios observed in the products of Table I when **2c** and **2d** are used. We suggest that a small contribution from an S_N1 pathway leads to what little alkene product is observed.

One can also assume that the data plotted in Figure 1 do not form a straight line and then attempt to explain the supposed curvature. A partial mechanism change is the most common source of Hammett curvature.[7,8] As an example, at the left in Figure 1 the major nucleophile might be free benzoic acid, but at the right a significant contribution of benzoate ion is possible. Our attempts to measure rates with benzoate ions were unsuccessful because the rates were immeasurably fast even at room temperature. However, no evidence for carboxylate carbonyl stretches in the infrared experiments was observed, but they could have been below the sensitivity of our measurements. The acid dimer equilibrium might also be involved. Another possible source of error and/or curvature could be changes in the fluidities of the viscous salts as a function of acid concentration or extent of reaction. Our results are most easily explained by nucleophilic attack at carbon but attack in part at phosphorus could also skew more points. We are unable to determine the importance of these factors with the information we presently have, nor is that our primary goal.

Conclusions

Oxyphosphonium salts **2** and their analogues appear to be excellent synthetic alternatives for formation of ethers, thioethers, esters, amines and alkyl halides. Their toxicity has not been studied but their low volatility makes them superior to the alternatives: $CH_3SO_3CF_3$, CH_3SO_3F, $CH_3OSO_3CH_3$, and CH_2N_2. Perhaps more significant are the potential uses of the secondary alkylating reagents. Experiments are underway to test conditions for reduced elimination and to extend the reactions to a wider variety of oxyphosphonium salts and functional groups to be alkylated.

The mechanistic information, taken from Arbusov reaction precedent[3] and from kinetic data in Table II, strongly suggests S_N2 reactivity for salts **2** with nucleophiles. The amount of octenes predicts that a more substantial substituent effect on the reactivity of **2d** should be observed. That **2c** should react faster than **2a** by an S_N2 mechanism is puzzling and inconsistent with the data from reactions of various trialkyl phosphites with methyl iodide,[3,12] although their conclusions come from intramolecular competition studies. The effects of our strongly ionizing media and the protons present are still to be determined since they are likely to play some role.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer 283 spectrometer with a Model 3600 data station. Proton NMR spectra were recorded on a Varian EM 360 in $CDCl_3$ relative to Me_4Si. They are reported as follows: chemical shift, integration, multiplicity, spin–spin coupling constants. Separations, accomplished by gas chromatographic analysis, used a Hewlett-Packard 5730A instrument equipped with FID and $^1/_8$ in. × 10 ft columns (20% SF96 on Chromosorb W 60/80 mesh, N_2 carrier at 40 mL/min) using the temperature program (initial 60 °C for 4 min, followed by 8 °C/min to 220 °C until all peaks eluted) capability. Liquid chromatographic separations were accomplished by using a medium pressure, fabricated system using an FMI Model RPSY pump (0–400 psi), $^1/_{16}$ in Teflon tubing and connectors (Alltech) and an Ace Glass glass column (1 cm i.d. × 25 cm L) equipped with an ISCO Model 226 absorbance monitor at 254 nm. The column was packed with 30-μm C_{18} reversed phase silica gel (Universal Scientific) and eluted with hexane–methylene chloride mixtures.

Hexanes (Fisher), methylene chloride (Fisher), methanol (Fisher), and anhydrous ether (Fisher) were used as obtained. Acetonitrile (Fisher) was distilled from calcium hydride immediately prior to use. Methyl, ethyl, and isopropyl phosphites (Aldrich) were distilled at reduced pressure and stored over 3-Å molecular sieves. Trimethyloxonium tetrafluoborate was purchased from Columbia Chemicals or prepared by the procedure of Meerwein.[9]

All products described in Table I had physical and spectral properties identical with authentic samples available commercially or by simple published procedures.[13]

Preparation of Tri-2-octyl Phosphite (1d). The general procedure of Ford-Moore and Perry[10] was used with 2-octanol in place of ethanol. However, pure phosphite was obtained only when care was taken to assure enough acid scavenger, accomplished simply by following the stoichiometry exactly. In fact, **1d** decomposes if a solution of it is washed with aqueous acid or concentrated aqueous ammonium chloride. Acidic decomposition of **1d** yields di-2-octylphosphonate, $(2\text{-octyl-O})_2P(=O)H$, clearly apparent in the IR spectrum from its P=O and P—H peaks. Phosphite **1d** was used in subsequent steps without further purification: IR (neat) 1030, 968, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (3 H, t), 1.31 (15 H, m), 4.15 (1 H, m).

Preparation of Methyltrimethoxyphosphonium Tetrafluoborate (2a). The procedure of Nesterov et al.[5] was used. To a solution of 3 g (0.02 mmol) of trimethyloxonium tetrafluoborate (TMOT) in 50 mL of methylene chloride in a 100-mL round-bottomed flask equipped with a condenser and N_2 inlet was added 2.36 g (0.019 mmol) of methyl phosphite over a 5-min period. The solvent begins to reflux before addition is complete. The clear solution is stirred for 3 h, any undissolved solids are filtered, and the solvent is removed by rotary evaporation to quantitatively yield a colorless, viscous oil: IR (neat) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (3 H, d, 17 Hz), 4.02 (9 H, d, 12 Hz). On a few occasions the salt contained varying but generally small amounts of phosphonate **3a**. Vigorously stirring or shaking the neat salt **2a** with 25-mL portions of either dry ether or pentane and decanting away the organic solvent left pure salt as determined by LC and NMR. The phosphonate **3** has no apparent affect on the yields and was generally only removed for the kinetic runs. Triphenyl phosphite was methylated with TMOT but is unreactive in the sense described herein.[14]

(12) Landauer, W. R.; Rydon, H. N. *J. Chem. Soc.* **1953**, 2224; *Chem. Ind. (London)* **1951**, 313.
(13) Vogel, A. "Textbook of Practical Organic Chemistry", 4th ed.; Longman Group Ltd.: London, 1978.

Preparation of Phosphonate 3a. Isolation of **3a** from the reaction of **2a** and methanol or from **1a** and CH_3I gave an identical product: IR (neat) 1320, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.55 (3 H, d, 15 Hz), 3.70 (6 H, d, 12 Hz). The characteristic P–CH_3 doublet occurs at the same chemical shift for **3b–d** and is useful for monitoring the purity of the salt **2**.

Methyltriethoxyphosphonium Tetrafluoborate (2b). The procedure of Nesterov et al.[5] described above for **2a** gave a colorless, viscous oil: IR (neat) 1050, 970 cm^{-1}; ^1H NMR ($CDCl_3$) 1.43 (9 H, t), 2.10 (3 H, d, 17 Hz), 4.42 (6 H, m).

Methyltriisopropoxyphosphonium Tetrafluoborate (2c). The procedure of Nesterov et al.[5] described above for **2a** gave a colorless, viscous oil: IR (neat) 1495, 1485, 1030, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48 (18 H, t), 2.13 (3 H, d, 18 Hz), 4.89 (3 H, m).

Methyltri-2-octoxyphosphonium Tetrafluoborate (2d). The procedure of Nesterov et al.[5] described above for **2a** gave a colorless, viscous oil: IR (neat) 1055, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (9 H, t), 1.37 (45 H, m), 2.16 (3 H, d, 17 Hz), 4.88 (3 H, m).

General Procedure for Alkylation of Nucleophiles (Table I). Reactions identical with the one described below were conducted by using the nucleophiles in Table I. Those results are the average of at least three replicate runs. A single preparation of 3–4 g of **2** served as the starting material for many simultaneous reactions.

A 0.225-g (1.0 mmol) portion of **2a** was added to an oven-dried 50-mL round-bottomed flask and to it was added 0.100 g (1.0 mmol) of cyclohexylamine that had been distilled and stored over anhydrous, potassium hydroxide. The flask was purged with dry nitrogen and sealed with a rubber septum. The flask got warm to the touch immediately after the addition but was nonetheless placed in a 25 °C oil bath for 12 h. A 1-mL portion of methanol was added, and the solution stirred for 30 min and analyzed by gas chromatography. Quenching with ethanol instead of methanol gave no discernable difference.

Kinetics of Reactions of 2a and 2c with Benzoic Acids. A liquid sample holder cell (45° KRS reflector plate) mounted on a Wilkes modified internal reflectance MIR Model 9 reflection system was used in conjunction with a Perkin-Elmer 283 infrared equipped with a Model 3600 datastation. The region between 1600 and 1900 cm^{-1} was scanned and recorded. Each data point (absorbance of C=O stretch at time, t) is the average of three absorbance readings taken consecutively over about 3 min. The data station allowed subtraction of the carboxylic acid spectrum that was previously recorded and stored on a disk. Better reproducibility at short times (low absorbance) encouraged the use of corrected data and the results in Table II are all corrected.

The pseudo-first-order kinetics were measured on samples prepared as follows. To a weighed sample of salt (approximately 1 mL) in a 25-mL round-bottomed flask equilibrated to 40 °C in a constant-temperature oil bath was added a weighed sample (2–4 mol %) of the nucleophile. The sample was stirred for a few minutes to assure homogeneity and transferred to the temperature equilibrated cell (40 ± 0.2 °C). Kinetics were run for 3–6 half-lives by measuring the ester absorbance (average of three determinations) after correction for the acid absorbance. Conversion of absorbance to concentration using calibration curves and the plotting of data gave straight lines from which k_1 was extracted:

$$(1)\ \frac{d[ester]}{dt} = k_1[2][acid] \text{ where } [acid]_t + [ester] = [acid]_0$$

$$(2)\ \frac{d[ester]}{[acid]_0 - [ester]} = k_1[2]dt$$

$$(3)\ \log [acid]_0 - (\log ([acid]_0 - [ester])) = -k_1[2]t$$

The second-order kinetics in acetonitrile were measured as follows. A solution of salt **2** in dry acetonitrile (0.2–0.4 M) was prepared in a 10-mL volumetric flask and equilibrated in a Neslab RTE8 bath at 40 ± 0.1 °C. A weighed sample of nucleophile approximately equal to **2** was added and the solution mixed. Aliquots were removed and added to the equilibrated MIR cell for absorbance measurement. Three replicas of each corrected absorbance were averaged and the results plotted by using the relationship below:

$$(4)\ \frac{d[ester]}{dt} = k_2[2][acid]$$

where $[acid]_t + [ester] = [acid]_0$ and $[2]_t + [ester] = [2]_0$

$$(5)\ \frac{d[ester]}{([acid]_0 - [ester])([2]_0 - [ester])} = k_2dt$$

$$(6)\ \left(\frac{1}{[2]_0 - [acid]_0} \log \frac{([2]_0 - [ester])}{([acid]_0 - [ester])}\right) - \frac{1}{[2]_0} \log \left(\frac{[2]_0}{[acid]_0}\right) = k_2t$$

A plot of the left side of (6) vs. time gave k_2 as the slope directly. All observed rate constants were measured at least 3 times and data in Table II are average values. Standard deviations were all generally 10–15%.

Registry No. **1a**, 121-45-9; **1b**, 122-52-1; **1c**, 116-17-6; **1d**, 7598-65-4; **2a**, 15294-11-8; **2b**, 18252-36-3; **2c**, 93000-48-7; **2d**, 93000-50-1; **2** (R = Ph), 2729-74-0; **3a**, 756-79-6; **4**, 111-87-5; **5** (R = CH_3), 929-56-6; **5** (R = 2-propyl), 68975-45-1; **6**, 67-56-1; **7** (R = CH_3), 115-10-6; **7** (R = Et), 540-67-0; **7** (R = 2-propyl), 598-53-8; **7** (R = 2-octyl), 1541-09-9; **8**, 108-98-5; **9** (R = CH_3), 100-68-5; **9** (R = 2-propyl), 3019-20-3; **10**, 65-85-0; **11** (R = CH_3), 93-58-3; **11** (R = 2-propyl), 939-48-0; **12**, 532-32-1; **13**, 503-74-2; **14** (R = CH_3), 556-24-1; **14** (R = 2-propyl), 32665-23-9; **15**, 539-66-2; **16**, 108-91-8; **17**, 142-84-7; TMOT, 420-37-1; (2-octyl-*O*)$_2$P(=O)H, 1809-13-8; $(C_6H_5O)_3P$, 101-02-0; $(C_6H_5O)_2P(CH_3)OCH_3$, 48170-06-5; C_6H_5OH, 108-95-2; $O{=}P(CH_3)(OC_6H_5)_2$, 7526-26-3; $C_6H_5OCH_3$, 100-66-3; 4-$NO_2C_6H_4CO_2H$, 62-23-7; 4-$CNC_6H_4CO_2H$, 619-65-8; 4-*t*-$BuC_6H_4CO_2H$, 98-73-7; 4-$CH_3C_6H_4CO_2H$, 99-94-5; 4-$CH_3OC_6H_4CO_2H$, 100-09-4; 4-$NO_2C_6H_4CO_2CH_3$, 619-50-1; 4-$CNC_6H_4CO_2CH_3$, 1129-35-7; 4-$CH_3C_6H_4CO_2CH_3$, 99-75-2; 4-$CH_3OC_6H_4CO_2CH_3$, 121-98-2; 4-$NO_2C_6H_4CO_2Pr$-*i*, 13756-40-6; 4-$CNC_6H_4CO_2Pr$-*i*, 29240-33-3; 4-$CH_3C_6H_4CO_2Pr$-*i*, 19277-55-5; 4-*t*-$BuC_6H_4CO_2Pr$-*i*, 67952-56-1; 1,8-bis(dimethylamino)-naphthalene, 20734-58-1; 2,6-lutidine, 108-48-5; 2-octanol, 123-96-6; methyl(cyclohexyl)amine, 100-60-7; isopropyl(cyclohexyl)amine, 1195-42-2; methyldipropylamine, 3405-42-3; isopropyldipropylamine, 60021-89-8; dimethyl(cyclohexyl)amine, 98-94-2; diisopropyl(cyclohexyl)amine, 93000-51-2.

(14) The salt **2** from $(C_6H_5O)_3P$ + TMOT reacted with methanol by apparent alcohol exchange at phosphorus, a reaction with precedent.[3] GC analysis showed large amounts of phenol and some anisole that apparently arises by alkylation after exchange.

$$(C_6H_5O)_3PCH_3 + CH_3OH \rightarrow (C_6H_5O)_2P(CH_3)OCH_3 + C_6H_5OH \rightarrow O{=}P(CH_3)(OC_6H_5)_2 + C_6H_5OCH_3$$

Halide ions give no apparent reaction.