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The Synthesis and Solvolysis of 1-Phenylethyl Disubstituted Phosphinates[1]

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A series of 1-phenylethyl esters of phosphinic acids has been prepared and their mode of solvolysis studied. Correlation of the rate constants for the solvolysis of 1-arylethyl diphenylphosphinates in 80% ethanol-water at 75° with σ^+ constants gave a ρ of -5.10, demonstrating that alkyl-oxygen fission occurs. This value is compared with the value obtained from other 1-arylethyl esters and chlorides. The rate data for the solvolysis of 1-phenylethyl esters: diphenylphosphinate (**1**), phenylphosphinate (**2**), methylphenylphosphinate (**3**), bis(*m*-nitrophenyl)phosphinate (**4**), diisopropylphosphinate (**5**), and dimethylphosphinate (**6**) are compared to the rates of other 1-phenylethyl esters and halides under the same conditions. Products from the solvolysis of **2** are compared to the products obtained from 1-phenylethyl chloride (**7**) under the same conditions (80% ethanol-water, 75°). The solvolysis of **5** showed an acid-catalyzed component. The products from the solvolysis of **1**, **2**, and **5** in 25% ethanol-water at 75° were 3% styrene, 12% 1-phenylethyl ethyl ether, and 85% 1-phenylethanol, which agrees well with the conclusion that a common carbonium ion is formed in each case and forms products independent of the phosphinate from which it originated.

Although there are a large number of leaving groups in solvolysis reactions, there has been little attention focused on the development of leaving groups whose reactivity is intermediate between *p*-nitrobenzoates (PNB) and chlorides. In measuring the rates of a series of compounds undergoing solvolysis there may be a tremendous range of reactivity and it would be very desirable to have a reasonably spaced range of reactivity of leaving groups available. Gaps in the present series are conveniently filled by phosphinate esters.

In order to investigate the relative rates of solvolysis of phosphinate leaving groups with respect to other leaving groups, various esters of 1-phenylethanol were synthesized. This system was chosen so that the solvolytic reactivity could be studied under mild conditions. The literature also contains abundant rate data on a variety of 1-phenylethyl chlorides, bromides, nitrates, acetates, tosylates, and *p*-nitrobenzoates which can be compared to the solvolysis rates for the phosphinates.

Correlation of the rates of solvolysis of the 1-arylethyl diphenylphosphinates with the σ^+ electrophilic substituent constants of Brown and Okamota[2] provide the desired evidence to demonstrate alkyl-oxygen fission.

Results and Discussion

The 1-arylethyl esters of diphenylphosphinic acid were prepared by the reaction of chlorodiphenylphosphine with the appropriate alcohol followed by oxidation of the phosphorus from the trivalent to the pentavalent state. The substituent groups in the alcohol moiety were *p*-methyl, *p*-chloro, *m*-chloro, and *p*-nitro. The rates of solvolysis of these esters are presented in Table I. The fact that the rates of formation of the phosphinic acid showed good first-order kinetics and that the rates of solvolysis correlate very well with σ^+ with a ρ value of -5.10 substantiate the premise that alkyl-oxygen fission with formation of a carbonium ion is occurring.

The values of ρ obtained for other 1-phenylethyl systems are presented in Table II. The large negative ρ values indicate that a substantial positive charge is formed in the transition state of each of the solvolysis reactions. The large negative ρ value for substituted 1-phenylethyl chlorides agrees well with the conclusion drawn by Shiner[3] from deuterium isotope effects that the more reactive chlorides solvolyze by an S_N1 mechanism with very little nucleophilic participation by solvent.

Based on the observation from Table II that even the very slow solvolysis of 1-phenylethyl acetates remains S_N1 in mechanism, the various other phosphinates can be presumed to solvolyze by the same mechanism.

With two exceptions all the phosphinates studied showed excellent first-order behavior. The rate of hydrolysis of 1-phenylethyl phenylphosphinate (**2**) was found to be sensitive to the addition of base. Competing S_N1 solvolysis and a basic hydrolysis mechanism have been identified in the reaction of **2**;[4] a pH

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[1] Supported in part by a grant from the National Science Foundation, GP-6133X.

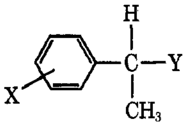
[2] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[3] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, **90**, 418 (1968).

[4] D. S. Noyce and J. A. Virgilio, *J. Org. Chem.*, **37**, 1052 (1972).

TABLE I

THE RATES OF SOLVOLYSIS OF 1-PHENYLETHYL ESTERS AND HALIDES IN ETHANOL–WATER MIXTURES (v/v)

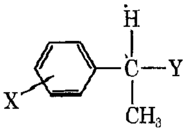


Registry no.	Run no.	X	Y	Solvent, %, EtOH–H₂O	Temp, °C	k, sec⁻¹
34887-65-5	1	H	$O_2P(C_6H_5)_2$	80	75.0	8.32×10^{-6}
	2	H	$O_2P(C_6H_5)_2$	80	90.0	4.83×10^{-5}
	3	H	$O_2P(C_6H_5)_2$	30	75.0	3.32×10^{-4}
34887-66-6	4	p-CH_3	$O_2P(C_6H_5)_2$	80	75.0	3.71×10^{-4}
34887-67-7	5	p-Cl	$O_2P(C_6H_5)_2$	80	75.0	4.93×10^{-6}
34887-68-8	6	m-Cl	$O_2P(C_6H_5)_2$	30	75.0	6.21×10^{-6}
	7	m-Cl	$O_2P(C_6H_5)_2$	50	75.0	1.52×10^{-6}
	8	m-Cl	$O_2P(C_6H_5)_2$	80	75.0	1.04×10^{-7} [a,b]
34887-69-9	9	p-NO_2	$O_2P(C_6H_5)_2$	80	110.0	Very slow
33521-92-5	10	H	$O_2P(H)C_6H_5$	80	75.0	5.73×10^{-5}
34887-71-3	11	H	$O_2P(C_6H_4$-m-$NO_2)_2$	80	75.0	1.52×10^{-3}
34887-72-4	12	H	$O_2P(CH_3)C_6H_5$	80	75.0	3.08×10^{-6}
34887-73-5	13	H	$O_2P(CH_3)_2$	80	75.0	1.03×10^{-6}
	14	H	$O_2P(CH_3)_2$	0	75.0	2.24×10^{-4} [c]
34887-74-6	15	H	$O_2P[CH(CH_3)_2]^2$	0	75.0	4.24×10^{-5} [d]
	16	H	$O_2P[CH(CH_3)_2]_2$	0	75.0	8.63×10^{-5} [e]
	17	H	$O_2P[CH(CH_3)_2]_2$	10	75.0	6.27×10^{-5} [e]
	18	H	$O_2P[CH(CH_3)_2]_2$	25	75.0	1.50×10^{-5} [e]
	19	H	$O_2P[CH(CH_3)_2]_2$	40	75.0	9.39×10^{-6} [e]
	20	H	$O_2P[CH(CH_3)_2]_2$	50	75.0	1.24×10^{-6} [e]
	21	H	$O_2P[CH(CH_3)_2]_2$	80	75.0	2.3×10^{-8} [a,f]
1524-12-5	22	H	O_2CCF_3	80	75.0	5.54×10^{-3} [d]
672-65-1	23	H	Cl	80	75.0	2.20×10^{-3} [d]
	24	H	Cl	30	25.0	4.90×10^{-3} [g]
2362-36-9	25	p-CH_3	Cl	95	25.0	3.82×10^{-5} [h]
	26	p-CH_3	Cl	80	25.0	5.89×10^{-4} [h]
	27	p-CH_3	Cl	60	25.0	6.30×10^{-3}
	28	p-CH_3	Cl	30	25.0	4.01×10^{-1} [a,i]
20001-65-4	29	p-Cl	Cl	30	25.0	5.82×10^{-4} [d]
34887-78-0	30	m-Cl	Cl	30	45.0	8.82×10^{-5} [d]
	31	m-Cl	Cl	30	75.0	3.30×10^{-3} [d]
	32	m-Cl	Cl	30	25.0	5.34×10^{-6} [j]

[a] Calculated from previous data using the Grunwald–Winstein correlation. [b] $m = 0.58$. [c] Measured at constant pH (7.0). [d] Measured at constant pH (7.5). [e] This rate constant is slightly too fast due to acid catalysis. [f] $m = 1.0$. [g] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1597 (1957). [h] Reference 3. [i] $m = 0.91$. [j] Calculated from previous data, $E_a = 26.5$.

TABLE II

THE VALUE OF ρ FOR THE SOLVOLYSIS OF 1-PHENYLETHYL ESTERS AND HALIDES



Y	Solvent	Temp, °C	ρ
$O_2P(C_6H_5)_2$	80% EtOH–H₂O	75.0	−5.10
$O_2P(H)C_6H_5$	30% EtOH–H₂O	45.0	−4.25
Cl	30% EtOH–H₂O	25.0	−6.89
O_2CCH_3 [b]	30% EtOH–H₂O	25.0	−5.96 [a]

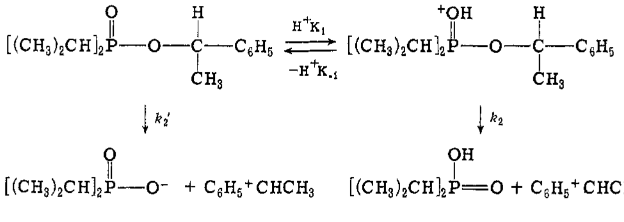
[a] E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Amer. Chem. Soc.*, 91, 7381 (1969). [b] Registry number: 93-92-5.

study has demonstrated that in acidic solution the predominant mechanism is S_N1 while in basic solution (above a pH of 9) the predominant mechanism is attack of hydroxide ion at phosphorus.

The solvolysis of **5** at a constant pH of 7.5 follows good first-order kinetics. In unbuffered solutions, the rate of solvolysis of **5** is not strictly first order but shows a weak autocatalytic component. The incursion of an acid-catalyzed path for **5** was not completely unexpected. In a homologous series of phosphinates in which the alkyl group is varied, the basicity of the phosphoryl oxygen should increase as the inductive effect of the alkyl groups increase. Thus in **5** the basicity of the phosphoryl oxygen has been increased by the two isopropyl groups to a point where it will be more readily protonated in acidic media.

The solvolytic reaction of **5** can be represented by Scheme I.

SCHEME I



The rate expression for this scheme can be expressed by eq 1.

$$\text{Rate} = k_2K[R_2P(O)OR][H^+] + k_2'[R_2P(O)OR] \qquad (1)$$

Since one of the kinetic runs was carried out at the constant pH of 7.5, the value of k_2' in water at 75° was determined to be 4.24×10^{-5} sec^{-1}. The value of k_2K was calculated from the rate of reaction at 60% completion to approximately equal 1.7×10^{-1}.

In view of the acid-catalyzed component observed for **5**, the products from the solvolysis of 1-phenylethyl diphenylphosphinate (**1**), of **2**, of **5**, and of 1-phenylethyl chloride (**7**) were analyzed to ensure that **5** was not solvolyzing by an abnormal mechanism. The SN1 solvolysis products for **2** in 80% ethanol–water at 75° consist of 60% 1-phenylethyl ethyl ether and 40% 1-phenylethanol, in close correspondence to the products observed for **7** under the same reaction conditions (53% ether and 47% alcohol). The products of the solvolysis of **5** in 25% ethanol–water at 75° were compared to the products obtained from **1** and **2**, which solvolyze by a SN1 mechanism under these conditions. The products from the solvolysis of **1**, **2**, and **5** were 3% styrene, 12% 1-phenylethyl ethyl ether, and 85% 1-phenylethanol. This agrees well with the conclusion that a common carbonium ion is formed in each case and forms products independent of the phosphinate from which it originated. Since the leaving group in the case of **5** is to some extent diisopropylphosphinic acid rather than the anion, the product distribution is not very sensitive to the change in charge type of the leaving group.

Several of the phosphinate esters, 1-phenylethyl methylphenylphosphinate (**3**) and **2**, are mixtures of diastereoisomers. However, a comparison of the nmr spectrum of the initial phosphinate and the phosphinate after 50% reaction for **2** showed that, within experimental accuracy, the ratio of diastereoisomers was unchanged. This implies that the two diastereoisomers are reacting at the same rate or that an equilibrium amount (through possible equilibrium of the trivalent species) is maintained.

Table III lists the relative rates of a large variety of leaving groups obtained from the solvolysis of the 1-phenylethyl system. Estimated rates are clearly labeled and should be used with caution, since they are derived from other systems and involve substantial extrapolation. Table III shows that the availability of leaving groups is quite diverse and extends over a range of reactivity of 10.[14]

As Table III shows, the phosphinate leaving groups are important in that they provide a graded reactivity series between the *p*-nitrobenzoate and chloride leaving group. In terms of availability, the diphenyl-, monophenyl-, and methylphenylphosphinates are easily prepared in high yield,[4] using dicyclohexylcarbodiimide.

TABLE III

THE RELATIVE RATES OF SOLVOLYSIS OF 1-PHENYLETHYL ESTERS AND HALIDES IN 80% ETHANOL–WATER AT 75°

$C_6H_5CH(CH_3)X$ X =	k, sec^{-1}	Relative rate	Footnotes
CH_3COO	3.1×10^{-9}	1.4×10^{-6}	*a*
p-$NO_2C_6H_4COO$	1.2×10^{-8}	5.5×10^{-6}	*b*
F	2×10^{-8}	9×10^{-6}	*c*
$[(CH_3)_2CH]_2POO$	2.3×10^{-8}	1.0×10^{-5}	This work
$(CH_3)_2POO$	1.03×10^{-6}	4.7×10^{-4}	This work
$C_6H_5(CH_3)POO$	3.08×10^{-6}	1.4×10^{-3}	This work
$(C_6H_5)_2POO$	8.32×10^{-6}	3.8×10^{-3}	This work
$C_6H_5(H)POO$	5.73×10^{-5}	2.6×10^{-2}	This work
(*m*-$NO_2C_6H_4)_2POO$	1.52×10^{-3}	6.9×10^{-1}	This work
Cl	2.20×10^{-3}	1.0	This work
CF_3COO	5.54×10^{-3}	2.5	This work
O_2NO	1.59×10^{-2}	7.2	*d*
Br	3.13×10^{-2}	14	*e*
I	2×10^{-1}	91	*b*
2,4,6-$(NO_2)_3C_6H_2O$	1.2	5.5×10^{2}	*f*
Tetra(1-phenylethyl)pyrophosphate	2.0	9.1×10^{2}	*g*
$CH_3S(O)_2O$	6.7×10	3.0×10^{4}	*h*
p-$CH_3C_6H_4S(O)_2O$	8.1×10	3.7×10^{4}	*i*
p-$NO_2C_6H_4S(O)_2O$	9.7×10^{2}	4.4×10^{5}	*j*
$CF_3S(O)_2O$	3.0×10^{5}	1.4×10^{8}	*k*

[a] Estimated from the ratio of rates for 1-phenylethyl acetate [E. A. Hill, *et al.*, *J. Amer. Chem. Soc.*, **91**, 7381 (1969)] and 1-phenylethyl phenylphosphinate in 30% ethanol-water and the rate of 1-phenylethyl phenylphosphinate in 80% ethanol-water. [b] Estimated from data for 1-*p*-anisylethyl *p*-nitrobenzoate in 70% acetone-water [H. L. Goering, R. G. Briody, and G. Sandrock, *J. Amer. Chem. Soc.*, **92**, 7401 (1970)] and in 80% ethanol-water [D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969)]. [c] Estimated rate obtained from A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 82. A Cl/F ratio of 10^5 and a Cl/I ratio of 10^{-2} were used to obtain the specific rates. [d] Calculated from data of Baker and Heggs [J. W. Baker and T. G. Heggs, *J. Chem. Soc.*, 616 (1955)]. [e] Calculated from data at other temperatures [A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1602 (1957)]. [f] Estimated from data of M. L. Sinnott and M. C. Whiting, *Chem. Commun.*, 1917 (1968), using a tosylate/picrate ratio of 8.5. [g] Estimated from data of G. O. Dudek and F. H. Westheimer, *J. Amer. Chem. Soc.*, **81**, 2641 (1959); 10^3 benzyl. [h] Estimated from data of P. K. Crossland, S. R. Hartshorn, and V. J. Shiner, Jr., Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 29, 1971, #40, using a ratio of 3×10^4 for mesylate/Cl ratio. [i] Estimated from data of H. M. R. Hoffman, *J. Chem. Soc.*, 6753, 6762 (1965). [j] Estimated from typical tosylate/nosylate ratios. [k] Estimated from data of T. M. Su, N. F. Sliwinski, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5386 (1969), using a OTF/OTOS ratio of 3×10^4.

There have been a number of studies on the rates of solvolysis of other phosphinate esters.[5-9] However, conclusive mechanism studies are often incomplete. In the homologous series of esters which have been studied, the compounds that solvolyze by an SN1 mechanism can be easily detected, for they have an unusually rapid rate and a lower (less negative) entropy value. By these criteria *tert*-butyl ethylphosphinate, *sec*-butyl bis(chloromethyl)phosphinate,[6] and allyl bis(chloromethyl)phosphinate[7] definitely solvolyze by an SN1 mechanism. The substitution of two chloromethyl groups in phosphinates promotes SN1 reactions by making the phosphinate leaving group a much weaker base.

Further evidence for carbonium ion formation in heterolysis is shown in the very recent studies by Haake and Diebert[10] on pyrolysis of phosphinate esters.

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(5) V. E. Bel'skii, G. Z. Motygullin, V. N. Eliseenkov, and N. I. Rizpolozhenskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 565 (1970); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 520 (1970).

(6) V. E. Bel'skii, M. V. Efremova, I. M. Shermergorn, and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 307 (1969); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 263 (1969).

(7) V. E. Bel'skii, M. V. Efremova, and Z. V. Lustina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1293 (1969), *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1192 (1969).

(8) V. E. Bel'skii, M. V. Efremova, and I. M. Shermergorn, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1654 (1966); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1597 (1966).

(9) V. E. Bel'skii, M. V. Efremova, and A. R. Panteleeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2278 (1968); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2154 (1968).

(10) P. Haake and C. E. Diebert, *J. Amer. Chem. Soc.*, **93**, 6931 (1971).

They found that *tert*-butyl diphenylphosphinate suffered pyrolysis 7000 times more rapidly than isopropyl diphenylphosphinate, and suggested a carbonium ion intermediate for the pyrolysis.

Thus, carbon–oxygen heterolysis is a reasonably prevalent mode of reaction for phosphinate esters, particularly in structural situations where the alkyl moiety provides a modest stabilization for the carbonium ion.

Experimental Section[11]

Materials.—Chlorodiphenylphosphine, dichlorophenylphosphine, phenylphosphinic acid, and 1-phenylethanol are commercially available. The appropriately substituted 1-phenylethanols were synthesized from the corresponding acetophenone by sodium borohydride reduction. Substituted 1-phenylethyl chlorides were obtained from the corresponding alcohol by reaction with thionyl chloride or phosphorus chlorides.

1-Phenylethyl Diphenylphosphinate (1).—To a stirred solution of 5.0 g (0.023 mol) of chlorodiphenylphosphine (Aldrich) and pyridine (1.8 g, 0.023 mol) in 300 ml of anhydrous ether was added 2.8 g (0.023 mol) of 1-phenylethanol (Aldrich). After refluxing for 1 hr, the solution was allowed to cool for 30 min and 10.0 g (0.023 mol) of lead tetraacetate (Matheson Coleman and Bell) was added in small portions. The mixture was refluxed for 1 hr and after cooling to room temperature the solution was filtered. The filtrate was washed with 2 × 200 ml of water and the resulting colorless oil was crystallized from mixed hexanes–ether, giving 3.50 g (49%) of ester **1**, nmr ($CDCl_3$) δ 7.5 (m, 15), 5.5 (2 q, 1), and 1.65 (d, 3).

Anal. Calcd for $C_{20}H_{19}O_2P$: C, 74.60; H, 5.90; P, 9.62. Found: C, 74.46; H, 5.94; P, 9.58.

1-(*p*-Methylphenyl)ethyl Diphenylphospinate (8).—Ester **8** was synthesized by the same method as **1** using 1-(*p*-methylphenyl)ethanol. The ester was isolated as a colorless oil after chromatography, nmr ($CDCl_3$) δ 7.6 (m, 10), 7.1 (s, 4), 5.55 and 5.41 (2 q, 1), 2.23 (s, 3), 1.60 (d, 3).

Anal. Calcd for $C_{21}H_{21}O_2P$: C, 74.99; H, 6.29; P, 9.21. Found: C, 74.84; H, 6.15; P, 9.06.

1-(*p*-Chlorophenyl)ethyl Diphenylphospinate (9).—Similarly, from 1-(*p*-chlorophenyl)ethanol and chlorodiphenylphosphine, ester **9** was obtained in 40% yield, mp 68.5–70°, nmr ($CDCl_3$) δ 7.6 (m, 10), 7.2 (s, 4), 5.57 and 5.42 (2 q, 1), 1.60 (d, 3).

Anal. Calcd for $C_{20}H_{18}ClO_2P$: C, 67.33; H, 5.08; Cl, 9.94; P, 8.68. Found: C, 67.14; H, 4.95; Cl, 9.90; P, 8.53.

1-(*m*-Chlorophenyl)ethyl Diphenylphosphinate (**10**).—*n*-Butyllithium (12.4 ml, 1.6 *M* in *n*-hexane, 0.0178 mol, Foote Mineral) was added dropwise to a stirred solution of 1-(*m*-chlorophenyl)-ethanol (3.0 g, 0.019 mol) in 200 ml of anhydrous diethyl ether under nitrogen in a Dry Ice–acetone bath. After the addition was complete, chlorodiphenylphosphine (4.32 g, 0.0191 mol) was added dropwise and the solution was warmed to room temperature. After 30 min the solution was concentrated and the slurry was dissolved in 200 ml of ether. The solution was washed with a solution of 10 ml of hydrogen peroxide (30%) in 200 ml of water, followed by 2 × 200 ml of water. The ether extract was dried ($MgSO_4$), filtered, and concentrated to yield 6.63 g (97%) of ester **10**, nmr ($CDCl_3$) δ 7.5 (m, 14), 5.61 and 5.46 (2 q, 1), and 1.32 (d, 3).

Anal. Calcd for $C_{20}H_{18}ClO_2P$: C, 67.33; H, 5.08; Cl, 9.94; P, 8.68. Found: C, 67.24; H, 4.98; Cl, 9.89; P, 8.58.

1-(*p*-Nitrophenyl)ethyl Diphenylphosphinate (11).—Ester **11** was synthesized by the same method as **1** using 1-(*p*-nitrophenyl)-ethanol. The resulting colorless oil was purified by crystallization from mixed hexanes to yield 58% of ester **11**, mp 101.5–102.5°, nmr ($CDCl_3$) δ 7.7 (m, 14), 5.70 and 5.50 (2 q, 1), and 1.65 (d, 3).

Anal. Calcd for $C_{20}H_{18}NO_4P$: C, 65.40; H, 4.94; N, 3.81; P, 8.43. Found: C, 65.15; H, 4.98; N, 3.97; P, 8.40.

Bis(*m*-nitrophenyl)phosphinic Acid (12).—The method of Dorken[12] was used with modifications. Chlorodiphenylphosphine (10 g, 0.046 mol) was added very cautiously to 20 ml of concentrated sulfuric acid at 0°. After the vigorous oxidation had subsided, 20 ml of 90% nitric acid was added dropwise over a period of 30 min. After stirring at room temperature for 2 hr the solution was poured onto an ice–water mixture. The white solid was filtered and dried to yield 4.5 g (45%) of bis(*m*-nitrophenyl)-phosphinic acid, mp 260–270°. Recrystallization from glacial acetic acid yielded 4.0 g of bis(*m*-nitrophenyl)phosphinic acid, mp 268–270° (lit.[12,13] mp 268° and 271–273°).

1-Phenylethyl Bis(*m*-nitrophenyl)phosphinate (13).—A solution of bis(*m*-nitrophenyl)phosphinic acid (5.0 g, 0.016 mol), *N*,*N*′-dicyclohexylcarbodiimide (3.3 g, 0.016 mol), and 1-phenylethanol (1.95 g, 0.016 mol) in 200 ml of anhydrous benzene was refluxed for 18 hr. After the solution had cooled to room temperature, the *N*,*N*′-dicyclohexylurea was removed by filtration and the benzene was removed on a rotary evaporator. The colorless oil was dissolved in 100 ml of diethyl ether and a small amount of solid material was removed by filtration. The ether was removed on a rotary evaporator to yield 4.0 g (66%) of ester **13**: mp 97–100°; nmr ($CDCl_3$) δ 7.7 (m, 8), 7.5 (m, 5), 5.65 (m, 1), and 1.75 (d, 3).

Anal. Calcd for $C_{20}H_{17}N_2O_6P$: C, 58.26; H, 4.15; N, 6.79; P, 7.52. Found: C, 58.37; H, 4.21; N, 6.83; P, 7.64.

1-Phenylethyl Phenylphosphinate (14)[4].—Ester **14** was synthesized in the same manner as ester **13**, yield 99%.

Methylphenylphosphinyl Chloride.—The method of Mislow[14] was used without modification.

1-Phenylethyl Methylphenylphosphinate (15).—1-Phenylethanol (3.6 g, 0.029 mol), methylphenylphosphinyl chloride (5.0 g, 0.029 mol), and pyridine (2.4 g, 0.03 mol) were dissolved in 100 ml of dry diethyl ether and the solution was refluxed for 1 hr. After the solution cooled, the pyridine hydrochloride was removed by filtration and the ether was removed on a rotary evaporator. The resulting colorless oil was passed through a silica gel column first using mixed hexanes followed by a solution of 50% ether–mixed hexanes which eluted 3.5 g (45.5%) of 1-phenylethyl methylphenylphosphinate (**15**), nmr ($CDCl_3$) δ 7.5 (m, 10), 5.4 (m, 1), 1.5 (m, 6).

Anal. Calcd for $C_{15}H_{17}O_2P$: C, 69.22; H, 6.59; P, 11.90. Found: C, 69.39; H, 6.41; P, 11.99.

Tetramethyldiphosphine Disulfide.—The method of Pollart and Harwood[15] was used without modification.

Dimethylphosphinyl Chloride.—The method of Pollart and Harwood[15] was used with modifications. Tetramethyldiphosphine sulfide (31.5 g, 0.17 mol) was suspended in 500 ml of methylene chloride and thionyl chloride (71.4 g, 0.60 mol) was added dropwise over a period of 1 hr. After the addition was complete, the solution was stirred for 1 hr. The solution was filtered, concentrated, and distilled to yield 23.0 g (60%) of dimethylphosphinyl chloride: bp 95° (20 mm); mp 66–68°; highly hydroscopic solid (lit.[16] mp 66.8–68.4°, bp 202–204°); nmr (CCl_4) δ 2.08 (d, $J_{CH_3P} = 14$ Hz).

1-Phenylethyl Dimethylphosphinate (16).—To a stirred solution of 1-phenylethanol (6.23 g, 0.050 mol) in 200 ml of anhydrous diethyl ether under nitrogen in a Dry Ice–acetone bath was added dropwise over 15 min 32 ml of *n*-butyllithium (1.6 *M* in *n*-hexane, 0.10 mol, Foote Mineral). After the addition was complete, dimethylphosphinyl chloride (5.75 g, 0.051 mol) was added dropwise and the solution was stirred for 30 min. The solution was warmed to room temperature and the ether was removed on a rotary evaporator. The residue was dissolved in 100 ml of methylene chloride, the solution was filtered and concentrated, and the residual oil was passed through a silica gel column using mixed hexanes, 20% ether–mixed hexanes, 40% ether–mixed hexanes, 60% ether–mixed hexanes, 80% ether–mixed hexanes, ether, and finally 20% methylene chloride–ether, which eluted 1.8 g (18%) of ester **16**, nmr (CCl_4) δ 7.37 (s, 5), 5.64 and 5.54 (2 q, 1), 1.83 (d, 3), 1.10 (d, 3, $J = 14$ Hz, PCH_3) and 1.10 (d, 3, $J = 14$ Hz, PCH_3). Ester **16** adhered to the column much more tenaciously than any of the previous phosphinates or the alkylaryl phosphinates.

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[11] Melting points and boiling points are uncorrected. Routine infrared spectra were obtained using a Perkin-Elmer Infracord Model 137. Nmr spectra were obtained using a Varian A-60, T-60, or HA-100 instrument with tetramethylsilane as the internal standard. The elemental analyses were carried out by the Microanalytical Laboratory of the University of California at Berkeley.

(12) C. Dorken, *Ber.*, **21**, 1505 (1888).

(13) G. O. Doak and L. D. Freedman, *J. Amer. Chem. Soc.*, **73**, 5658 (1951).

(14) O. Korpium, R. Lewis, J. Chickos, and K. Mislow, *ibid.*, **90**, 4843 (1968).

(15) K. A. Pollart and H. J. Harwood, *J. Org. Chem.*, **27**, 4444 (1962).

(16) G. M. Kosolapoff and R. M. Watson, *J. Amer. Chem. Soc.*, **73**, 5466 (1951).

Diisopropylphosphine Oxide.—The method of Crofts and Kosolopoff[17] was used with modifications. Magnesium (97.2 g, 4.0 mol) was placed in 1500 ml of dry diethyl ether under nitrogen and isopropyl bromide (492.0 g, 4.0 mol) was added dropwise at such a rate as to maintain a constant reflux of ether. After the addition was complete and visible reaction had ceased, diethyl phosphonate (160.0 g, 1.16 mol, Aldrich) was added over a period of 4 hr. The mixture was stirred for 12 hr and then refluxed for 1 hr. After the addition of a saturated solution of ammonium chloride (500 ml), the ether layer was separated and the aqueous phase was extracted with 3 × 500 ml of methylene chloride. The combined extracts were dried ($MgSO_4$), filtered, and concentrated, and the colorless oil was distilled to yield 97.0 g (63%) of diisopropylphosphine oxide: bp 188° (30 mm) [lit.[18] bp 54–55° (1.5 mm)]; nmr ($CDCl_3$) δ 1.1 (m, 12), 2.0 (m, 2), and two triplets at 2.7 and 11.6 (total 1 H, J = 633 Hz, PH, and J = 3 Hz, PH, CH).

Diisopropylphosphinic Acid.—The method of Crofts and Kosolopoff[17] was used with modifications. Hydrogen peroxide (30%, 14 ml) was added cautiously with stirring to diisopropylphosphine oxide (10.0 g, 0.075 mol). Since the reaction was not very exothermic the solution was placed in an oil bath at 75° for 24 hr. The colorless oil was dissolved in 200 ml of diethyl ether, dried ($MgSO_4$), filtered, and concentrated to yield 9.7 g (87%) of diisopropylphosphinic acid: nmr ($CDCl_3$) δ 1.07 and 1.28 (2 d, 12, J = 16 Hz, PCH_3), 1.88 (m, 2), and 13.95 (s, 1). The acid was used without further purification.

Diisopropylphosphinyl Chloride. A.—Phosphorus pentachloride (13.5 g, 0.065 mol) was added in small portions to a solution of diisopropylphosphinic acid (9.7 g, 0.065 mol) in 200 ml of methylene chloride. After the addition was complete, the solution was stirred for 1 hr and the solution was concentrated. The yellow oil was distilled to yield 9.0 g (83%) of diisopropylphosphinyl chloride: bp 65° (0.2 mm) [lit.[19] bp 77° (3 mm)]; nmr ($CDCl_3$) δ 1.14 and 1.45 (2 d, 12, showing some fine splitting of about 2 cycles, J = 7 Hz, CH_3CH and J = 18 Hz, CH_3P), and 2.20 (m, 2).

B.—Diisopropylphosphine oxide (10.0 g, 0.075 mol) was dissolved in 200 ml of diethyl ether, and thionyl chloride (25.0 g, 0.15 mol) was added dropwise (caution: a very vigorous reaction occurs). After the addition was complete, the solution was stirred for 5 min and the ether and excess thionyl chloride were removed on a rotary evaporator. The yellow oil was distilled to yield 10.4 g (84%) of diisopropylphosphinyl chloride. The product is identical with that in part A.

1-Phenylethyl Diisopropylphosphinate (17).—To a stirred solution of 1-phenylethanol (2.20 g, 0.0178 mol) in 200 ml of anhydrous diethyl ether under nitrogen in a Dry Ice–acetone bath was added dropwise over 5 min 11 ml of *n*-butyllithium (1.6 *M* in *n*-hexane, 0.0178 mol, Foote Mineral). After the addition was complete, diisopropylphosphinyl chloride (3.0 g, 0.0178 mol) was added dropwise and the solution was warmed to room temperature. The solution was concentrated, and the slurry was dissolved in ether. The solution was filtered and concentrated, and the residual oil (4.0 g, 90% yield) was purified by chromatography on a silica gel column using mixed hexanes, 10% ether–mixed hexanes, 20% ether–mixed hexanes, 10% ether–mixed hexanes, 50% ether–mixed hexanes, 60% ether–mixed hexanes, 80% ether–mixed hexanes, ether, 10% methylene chloride–ether, and finally 20% methylene chloride–ether, which eluted 1.2 g (27%) of ester **17**, nmr ($CDCl_3$) δ 7.3 (s, 5), 5.55 (m, 1), 1.8 (m, 2), and 1.2 (m, 15). The methyl region was resolved on the HA-100 nmr ($CDCl_3$) of methyl region δ 1.23, 1.07, 0.94, and 0.78 (4 d, 12) and 1.52 (d, 3).

Anal. Calcd for $C_{14}H_{23}O_2P$: C, 66.12; H, 9.12; P, 12.19. Found: C, 65.94; H, 9.10; P, 12.04.

1-Phenylethyl Trifluoroacetate (18).—A solution of trifluoroacetic anhydride (21.0 g, 0.10 mol) in 100 ml of diethyl ether was added dropwise over a period of 1 hr to a solution of pyridine (7.9 g, 0.10 mol) and 1-phenylethanol (12.2 g, 0.10 mol) in 100 ml of ether. The reaction mixture was maintained at 0° by an ice–water bath. After the addition was complete and the solution had warmed to room temperature, the pyridinium trifluoroacetate was removed by filtration, and the ether was removed on a rotary evaporator. The clear oil was distilled to yield 16 g (78%) of ester **18**: bp 32° (0.5 mm); nmr ($CDCl_3$) δ 1.60 (d, 3), 5.99 (q, 1), and 7.32 (s, 5).

Anal. Calcd for $C_{10}H_9F_3O_2$: C, 55.04; H, 4.17. Found: C, 54.98; H, 4.36.

Kinetic Methods.—The procedures for the solvolysis rate measurements at nonconstant pH have been described.[20]

For kinetic measurements at constant pH the kinetic samples were prepared by weighing 0.0006 mol of phosphinate ester into a 50-ml vessel. To the vessel was added 50 ml of aqueous ethanol, and the entire vessel was suspended in the constant-temperature bath. If the run was unusually fast, the solvent was equilibrated to the appropriate temperature and the phosphinate in several milliliters of solvent was added. The acid produced was monitored by a pH-Stat (Radiometer Corp.) which consisted of a TTT 1c automatic titrator, a ABU 1c autoburette (with a 2.5 ml burette), a TTA 3c titrator assembly, and a 2c recorder.

The solution was maintained at the appropriate pH by the addition of 0.30 *M* potassium hydroxide in aqueous ethanol.

Product Analysis.—The analysis of products was carried out according to the glpc procedure of Buckson and Smith,[21] who analyzed the ethanolysis products from phenyldimethylcarbinyl chloride and phenyldimethylcarbinyl *p*-nitrobenzoate.

The peaks were identified by comparing retention times to those of dichloromethane solutions of pure samples. The molar responses of 1-phenylethyl ethyl ether, 1-phenylethyl alcohol, and styrene relative to that of 1-phenylethyl chloride, a convenient standard, were determined in separate experiments. In separate experiments it was shown that the alcohol, ether, and styrene were stable under the reaction conditions for *ca.* 10 half-lives.

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[17] P. C. Crofts and G. M. Kosolopoff, *J. Amer. Chem. Soc.*, **75**, 3379 (1953).

[18] M. I. Kabachnik and E. N. Tsvetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1227 (1963).

[19] A. A. Neimysheva and I. L. Knunyants, *Zh. Obshch. Khim.*, **36**, 1090 (1966).

[20] D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

[21] R. L. Buckson and S. G. Smith, *ibid.*, **32**, 634 (1967).