carbon tetrachloride–methylene chloride, giving 0.11 g (0.90 mmol, 30% yield) of II: mp 146–147°; nmr ($CDCl_3$) δ 2.66 (s, 2), 2.32 (s, 1); ir (KBr) 3000 (w), 1548 (s), 1433 (w), 1399 (m), 1386 (s), 1366 (s), 1241 (w), 1137 (w), 1102 (w), 1033 (m), 991 (s), 898 (w), 769 (w), and 668 cm^{-1} (s); uv max (95% EtOH) 278 mμ (ϵ 610), 217 (4300), end absorption; mass spectrum (70 eV) 123.0794 (calcd for $C_6H_9N_3^+$: 123.0796). *Anal.* Calcd for $C_6H_9N_3$: C, 58.52; H, 7.37; N, 34.12. Found: C, 58.29; H, 7.49; N, 33.96.

Photolyses of I and II were carried out in benzene and methylene chloride solutions in nmr tubes in the probe of a Varian HR-60 spectrometer. At ambient temperatures and with the probe cooled to −56° (cooled only for methylene chloride solution), irradiation (1000-W mercury lamp) of I gave material with an nmr spectrum identical with that of a mixture of 2-butyne and acetonitrile. The irradiations of I and II by medium pressure mercury arc also gave 2-butyne and acetonitrile, identified by identical nmr spectra and vpc retention times.

Pyrolyses of I and II were carried out in a flow system. At 300° I gave a mixture of II, 2-butyne, and acetonitrile. At the same temperature, II did not react. At higher temperaturs (*ca.* 500°), II also gave 2-butyne and acetonitrile. Products were identified by nmr and vpc as above.

Rate measurements on I were made in a Varian A-60A spectrometer equipped with a V-6040 variable temperature controller. Temperatures were determined by measuring the separation between the methyl and hydroxyl resonances in a separate methanol sample.[6] The methanol sample was used to determine the temperature before each sample spectrum. At least 15 min were allowed for thermal equilibration each time a tube was placed in the probe and each time the probe temperature was changed. Half-widths were measured and compared with computer-calculated values.[3] A linear least squares treatment gave the indicated activation parameters.

Registry No.—I, 33209-84-6; II, 33209-85-7.

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An Investigation of the Rate of Hydrolysis of 1-Phenylethyl Phenylphosphinate as a Function of pH[1]

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During our investigation of the solvolysis of a variety of phosphinate esters, we examined the mode of reaction of 1-phenylethyl phenylphosphinate (**1**) as a function of pH. The rate of reaction of **1** was found to be very sensitive to the addition of hydroxide ion. In order to determine the molecularity of the reaction, the rate of reaction of **1** as a function of pH was studied (Table I). The rates were measured in the presence of 0.10 *M* $NaClO_4$ to minimize salt effects.

The pH–rate profile for the solvolysis of **1** is shown in Figure 1. The interesting aspects of the curve are that between pH 4 and 6 there is a plateau and above pH 9 a linear plot with a slope of 1 is observed. The entire curve is reproduced very well by eq 1 where $k_1 = 1.58 \times 10^{-4}$ sec^{-1} and $k_2 = 2.63 \times 10^2$ M^{-1} sec^{-1}.

$$\text{rate} = k_1[1] + k_2[1][OH] \quad (1)$$

The comparison of the rates of hydrolysis of phosphonates,[2] $(RO)_2P(O)H$, and phosphinates,[3] $(RO)C_2H_5P(O)H$, which contain a P–H bond, has led to the conclusion that the enhanced rates of highly branched esters such as R = *tert*-butyl were attributable to the incursion of an SN1 mechanism. Since the 1-phenylethyl ester should be of the same order of reactivity and form a carbonium ion of the same stability as the *tert*-butyl group, the probable mechanism occurring in the plateau region of the curve is formation of a carbonium ion by an SN1 mechanism. In order to substantiate the SN1 nature of the reaction, the rates of solvolysis of 1-(*m*-chlorophenyl)ethyl phenylphosphinate ($k_1 = 9.45 \times 10^{-6}$ sec^{-1}), 1-(*p*-methylphenyl)ethyl phenylphosphinate ($k_1 = 8.28 \times 10^{-3}$ sec^{-1}), and the parent (**1**) ($k_1 = 2.95 \times 10^{-4}$ sec^{-1}) were measured in the acidic region in 30% ethanol–water (v/v) at 45.0°. The Hammett plot of the rate constants *vs.* Brown's σ^+ values gives a good correlation with a ρ of −4.25. This indicates that substantial positive charge is developed in the transition state and that the reaction in the acidic region does indeed follow a carbonium ion mechanism.

Recent investigations of alkaline hydrolysis have shown that phosphates,[4,5] phosphonates,[4] and phosphinates[6] hydrolyze by exclusive attack of the hydrox-

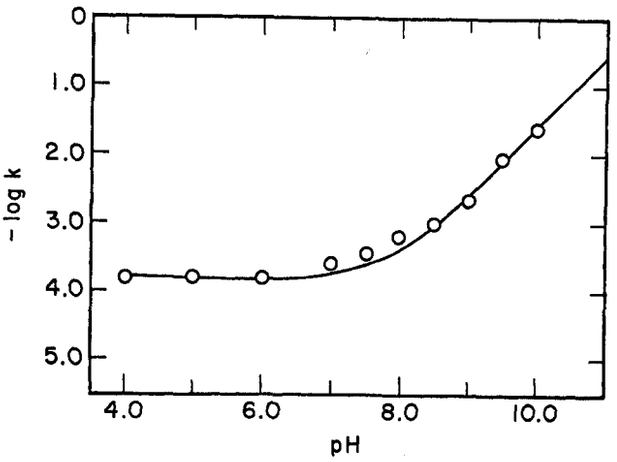

Figure 1.—pH–rate profile for the hydrolysis of 1-phenylethyl phenylphosphinate.

TABLE I
THE RATE OF REACTION OF 1 IN 30% ETHANOL–WATER (0.1 *M* $NaClO_4$) AT 45°

pH	Rate	Log *k*	Rel rate
4.0	1.60×10^{-4}	−3.796	1
5.0	1.55×10^{-4}	−3.809	1
6.0	1.58×10^{-4}	−3.801	1
7.0	2.46×10^{-4}	−3.609	1.6
7.5	3.48×10^{-4}	−3.458	2.2
8.0	6.42×10^{-4}	−3.192	4.1
8.5	8.05×10^{-4}	−3.094	5.1
9.0	2.06×10^{-3}	−2.686	13
9.5	9.06×10^{-3}	−2.043	57
10.0	2.44×10^{-2}	−1.613	154

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

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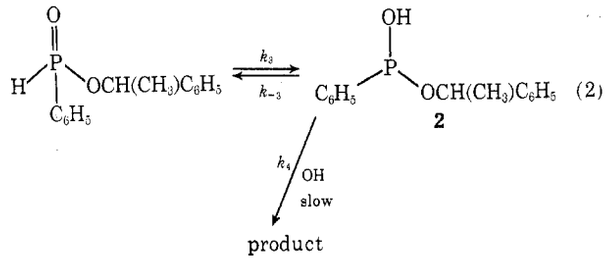
ide ion at phosphorus. By analogy to these and other studies the mechanism that is occurring in the basic region (above pH 9) is attack of hydroxide ion with the probable formation of a pentacoordinate intermediate (the formation of this intermediate has not been unambiguously established in the alkaline hydrolysis of noncyclic phosphorus compounds).

The high rate of reaction of **1** may be simply a more rapid rate due to the phosphorus atom being more liable to attack because of the lack of steric hindrance to the approaching hydroxide ion. A more attractive possibility is that the bimolecular reaction may be occurring through a trivalent species (eq 2) (*e.g.*, **2**). This mechanism implies that trivalent phosphorus esters would have an unusually fast rate of hydrolysis when compared to pentavalent compounds. This is substantiated by the rapid rate of hydrolysis of triethylphosphite (TEP) ($k_{10°} = 5.77 \times 10^{-3}$ sec^{-1}).[7] Comparison of the rate ratio of TEO to diethyl phosphonate



(2)

(DEP)[8] at 80° shows that the hydrolysis of the trivalent species is unusually fast (TEP/DEP = 4670). Assuming k_4 for **2** to be very similar to the rate of hydrolysis of TEP (4.3 sec^{-1} at 80°), the value of k_3/k_{-3} would then be approximately 2×10^{-5}. This is in agreement with physical observations that the trivalent species could not be detected by spectral techniques.[8]

Acid-catalyzed exchange of the hydrogen bound to phosphorus and the oxidation of dialkyl phosphonates has been found to occur through the phosphite form (trivalent species).[9-12] In these reactions the rate-determining step was found to be the formation of the trivalent species.

Thus the trivalent species is a very attractive intermediate in the alkaline hydrolysis of phosphinate esters containing a P–H bond. Further evidence will be needed to definitely establish this hypothesis.

Experimental Section[13]

Preparation of Materials. A. 1-Phenylethyl Phenylphosphinate.—*N*,*N*′-Dicyclohexylcarbodiimide (5.00 g, 0.0242 mol, Aldrich) was added to a refluxing solution of phenylphosphinic acid (3.44 g, 0.0242 mol, Aldrich) in 200 ml of anhydrous benzene. After refluxing for 30 min, 1-phenylethanol (2.96 g, 0.0242 mol) was added dropwise and the mixture was refluxed for 30 min. The solution was cooled to room temperature and *N*,*N*′-dicyclohexylurea was removed by filtration. 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. Removal of the ether on the rotary evaporator yielded 5.90 g (99%) of 1-phenylethyl phenylphosphinate as a colorless oil. The nmr spectrum[14] of the ester in chloroform-*d* showed bands at δ 7.3 (m, 10 H), 7.30 and 7.60 (2d, 1 H, J_{P-H} = 566 and 564 Hz), 1.55 and 1.63 (2 d, 3 H), and 5.60 (m, 1 H).

Anal. Calcd for $C_{14}H_{15}O_2P$: C, 68.35; H, 6.12; P, 12.58. Found: C, 68.18; H, 6.05; P, 12.46.

B. 1-(*p*-Methylphenyl)ethyl Phenylphosphinate.—1-(*p*-Methylphenyl)ethyl phenylphosphinate was synthesized in the same manner from 3.0 g (0.145 mol) of 1-(*m*-chlorophenyl)-ethanol to yield 6.06 g (96%) of the desired product. The infrared spectrum of the neat ester showed bands at 2370 (w), 1230 (s), 1125 (s), 955 (s), and 822 cm^{-1} (m). The nmr spectrum[14] of the ester in chloroform-*d* showed bands at δ 7.4 (m, 5 H), 7.18 (s, 4 H), 7.3 and 6.6 (2d, 1 H, J_{P-H} = 570 and 577 Hz), 1.48 and 1.61 (2d, 3 H, $CHCH_3$), 5.5 (m, 1 H), and 2.15 and 2.22 (2s, 3 H).

C. 1-(*m*-Chlorophenyl)ethyl Phenylphosphinate.—1-(*m*-Chlorophenyl)ethyl phenylphosphinate was synthesized in the same manner from 3.3 g (0.024 mol) of 1-(*p*-methylphenyl)-ethanol to yield 4.00 g (97%) of the desired product. The nmr spectrum[14] of the ester in chloroform-*d* showed bands at δ 7.5 (m, 9 H), 7.4 and 7.6 (2d, 1 H, J_{P-H} = 570 and 577 Hz), 1.62 and 1.72 (2d, 3 H) and 5.5 (m, 1 H).

Kinetic Methods.—Rates were measured by standard techniques (pH-Stat method) using a Radiometer automatic titration apparatus 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.

Registry No.—**1**, 33521-92-5; 1-(*p*-methylphenyl)-ethyl phenylphosphinate, 33521-93-6; 1-(*m*-chlorophenyl)ethyl phenylphosphinate, 33521-94-7.

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(14) The additional multiplicity in the nmr spectra is due to the presence of two diasteroisomers.

Spectrophotometric Determination of the Second Dissociation Constants of the Aminoisoquinolines

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The first protonation of nitrogen heterocycles containing amino substituents on the ring has been shown to occur at the ring nitrogen and not at the substituent amino group.[1-4] Albert[5] has compiled a large number of ionization constants corresponding to this first and second protonation as determined by various workers. In previous work done in this laboratory, we have updated or determined the second pK_a' values for the isomeric aminopyridines and aminoquinolines.[6] It is of interest to investigate the relative basicity of the primary amino group for the isomeric aminoisoquinolines (in terms of pK_a') by ultraviolet spectroscopy and compare their values to those obtained from the above pyridine and quinoline compounds. The second pK_a' values for the aminoisoquinolines along with the temperature at which they were determined are given in Table I.

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