When crystals separated on long standing, they were isolated by filtration and were identified by melting point and infrared data as *p*-chlorobenzoic acid. The filtrate was taken up in ether, washed with sodium bicarbonate solution, dried, and redistilled. The boiling point, index of refraction, and analysis for carbon and hydrogen were essentially unchanged. Infrared and ultraviolet absorption studies indicated the presence of an ester and an α,β-unsaturated carbonyl but no styrene-like configuration. An empirical formula of $C_{19}H_{20}Cl_2O_3$ was calculated from the analytical data.

Application of this same method to 22.16 g. (0.1 mole) of the O-ethyl derivative obtained in (*A*) above gave 7 g. of a yellow liquid which boiled at 86–90° (0.5 mm.), n_{D}^{25} 1.5203.

Anal. Calc'd for $C_{12}H_{13}ClO_3$: C, 59.90; H, 5.44. Found: C, 61.93; H, 5.58.

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A Comparison of the Electrophilic Reactivity of Styrene and Phenylacetylene

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It has been suggested that the relative reactivity of a comparable alkene-alkyne pair varies: with electrophilic reagents the alkene is more reactive; with nucleophilic reagents the alkyne is more reactive.[1] In order to provide a clear-cut example in the latter category, a qualitative comparison of the reactivity of phenylacetylene and styrene towards a nucleophilic reagent, methoxide ion, was made in the reactions

$$C_6H_5C{\equiv}CH + CH_3OH \xrightarrow{NaOCH_3} C_6H_5CH{=}CHOCH_3$$

$$C_6H_5CH{=}CH_2 + CH_3OH \xrightarrow{NaOCH_3} C_6H_5CH_2CH_2OCH_3 \quad \text{(I)}$$

In a recent study[2] it was established that the rate-limiting step in the first reaction was the addition of methoxide ion to phenylacetylene and that its half-life at 149° was about six hours for concentrations of 0.1 mole liter^{-1}.[1]

The preparation of I from styrene appears not to have been reported. When styrene was heated with sodium methoxide in methanol at 146–149° in sealed ampules it was found that after two days only traces of I had formed. After 10 or 20 days, however, the presence of this ether could be clearly demonstrated.

In order to eliminate $C_6H_5CH(OCH_3)CH_3$ (II) as a possible product from styrene, I and II were prepared by known procedures.[3,4] Infrared spectra of the products of the methoxide-catalyzed addition of methanol to styrene showed that the ether I, not II, had formed. In this connection it is interesting to note that the charge distribution in styrene must be remarkably sensitive to the nature of the attacking species, for styrene does give the ether II in methanol-sulfuric acid. Apparently the phenyl group can distribute charge best when the attack of either a free radical or a positive or negative species is on the β-carbon. Similar results obtain with phenylacetylene.[5,6]

By direct comparison, it is clear that phenylacetylene is more electrophilic than styrene in its reactivity toward the nucleophilic reagent sodium methoxide. This is in contrast to the greater nucleophilic reactivity of styrene toward free radicals[5] or bromine.[7]

EXPERIMENTAL

Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride optics: the liquid samples were measured as films between sodium chloride plates or in *ca.* 0.025 mm. sodium chloride cells; a reference sample of polystyrene was measured as a 0.007 mm. sheet.

1-Methoxy-2-phenylethane (I). This ether, prepared by the method of Deshapande,[3] was redistilled from sodium. The distillate had b.p. 81–82° (22 mm.), n_{D}^{22} 1.4971 [lit.[3] b.p. 68–70° (12 mm.), n_{D}^{24} 1.4970].

1-Methoxy-1-phenylethane (II). II was prepared by a procedure outlined in a patent.[4] A solution of 30 ml. of styrene, 3 ml. of 95% sulfuric acid, 100 ml. of methanol, and a few crystals of hydroquinone was made up in a flask with a long narrow neck. The flask was cooled in ice, its air space was blown out with nitrogen, and the flask neck was sealed. After 18 hours in a steam-bath, the solution was neutralized with ethanolamine, then treated with water and ether. The crude II obtained from the ether extract was distilled from sodium giving a practically quantitative yield of a liquid, n_{D}^{25} 1.4888–1.4920. For a middle fraction b.p. 71–76° (32 mm.), n_{D}^{25} 1.4911 [lit.[8] b.p. 88° (47 mm.), n_{D}^{25} 1.4905].

Anal. Calc'd for $C_9H_{10}O$: C, 79.36; H, 8.89. Found: C, 79.71; H, 9.01.

Methoxide-catalyzed addition of methanol to styrene. The reaction was carried out in 16 ml. of methanolic solution in Pyrex ampules at 146–150°. In a typical experiment the concentrations of styrene and sodium methoxide in the solution were 3 and 0.6 mole/liter^{-1} respectively. Before each ampule was sealed, it was cooled in Dry Ice and its vapor space was blown out with nitrogen. At the end of a fixed period the ampule was chilled and opened. The solution was poured off from the white solid, presumably polystyrene, washed with water, and then was dried over calcium chloride and potassium hydroxide. A reference sample of styrene was washed and dried by the same procedure. As the reaction progressed, more and more white solid was deposited and correspondingly less liquid product was recovered. Some of the results follow.

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(1) Raphael, *Acetylenic Compounds in Organic Synthesis*, Butterworth's Scientific Publications, London, 1955, p. 21.

(2) Miller and Shkapenko, *J. Am. Chem. Soc.*, **77**, 5038 (1955).

(3) Deshapande, *J. Indian Chem. Soc.*, **15**, 509 (1938).

(4) Stanley, Minkoff, and Youell, U. S. Patent 2,248,518 [*Chem. Abstr.*, **35**, 6598 (1941)].

(5) Kharasch, Jerome, and Urry, *J. Org. Chem.*, **15**, 966 (1950).

(6) Nef, *Ann.*, **308**, 264 (1899).

(7) Robertson, Dasent, Milburn, and Oliver, *J. Chem. Soc.*, 1628 (1950).

(8) Mislow, *J. Am. Chem. Soc.*, **73**, 4043 (1951).

Time at 146–149°	Recovered liquid	n_D^{20}
2 days	60%	1.5468[a]
10 days	<10%	1.5463
20 days	<10%	1.5530

[a] Unreacted styrene n_D^{20} 1.5467 (lit.[9] n_D^{20} 1.5465); polystyrene lit.[9] n_D^{20} 1.59–1.60.

An infrared spectrum showed that the liquid from the two-day ampule was essentially styrene, although traces (<5%) of polystyrene and I were present. Infrared spectra of the products of longer reaction time clearly indicated more polystyrene and I. The liquid products (*ca.* 2 ml.) from several ampules were combined and distilled at 1 mm. from the polystyrene. It was estimated from the refractive index of the distillate that after 10–20 days of reaction the ratio of styrene to I was still *ca.* 10:1. Some of the styrene was removed from the distillate under a vacuum and an infrared spectrum of the residue indicated more definitely the presence of I. The over-all yield of I was <2%.

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[9] Boundy and Boyer, *Styrene*, Reinhold Publishing Corp., New York, N. Y., 1952, pp. 57, 216, 450, and 525.

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Kinetics of Reaction of Acyl Chlorides. III. Hydrolysis of Phosphinyl Chlorides[1]

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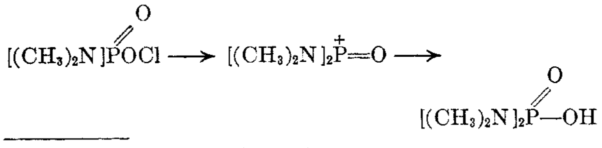
Recently Dostrovsky and Halmann[2] described a careful study of the kinetics of hydrolysis of dialkyl phosphochloridates, $(RO)_2POCl$. They concluded that these chlorides were prone to react by S_N2 mechanisms even in solvents of high ionizing power. As a continuation of our studies of the mechanisms of hydrolysis of acyl chlorides,[1] it was of interest to extend their study to N,N,N^1,N^1-tetramethylphosphorodiamidic chloride, $[(CH_3)_2N]_2POCl$ (I).

Table I presents the results of the kinetics experiments. I hydrolyzes at a rate almost identical to that of diisopropyl phosphochloridate at 20°. In contrast to the latter, however, the rate of hydrolysis is completely unaffected by added hydroxide ion, *m*-cresoxide ion, or pyrrolidine. This is strong evidence for an S_N1 mechanism of hydrolysis for the former:



$$[(CH_3)_2N]\overset{O}{\overset{/\!\!/}{P}}OCl \longrightarrow [(CH_3)_2N]_2\overset{+}{P}{=}O \longrightarrow [(CH_3)_2N]_2\overset{O}{\overset{/\!\!/}{P}}{-}OH$$

TABLE I

First Order Rate Constants for Hydrolysis of N,N,N^1,N^1-Tetramethylphosphorodiamidic Chloride in Water

Initial Conc'n Chloride $\times 10^3$, *M.*	Temp., °C.	Added Reagents, *M*	$k_1 \times 10^4$, sec.$^{-1}$
1.093	0.6	$NaClO_4$, 0.0463	5.05
1.085	15.0	$NaClO_4$, 0.0463	30.0
1.115	20.1	$NaClO_4$, 0.0463	52.0
3.09	20.1	NaOH, 0.0206	53.7
4.24	20.1	Pyrrolidine, 0.06425	57.3
1.355	20.1	*m*-Cresol, 0.0416 and NaOH, 0.0416	50.9
1.003	30.0	$NaClO_4$, 0.0463	141.7

If the reaction were proceeding by an S_N2 mechanism, N,N,N^1,N^1-tetramethylphosphorodiamidic chloride should react much more slowly than diisopropyl phosphochloridate, just as the latter reacts more slowly than diphenylphosphinyl chloride, $(C_6H_5)_2POCl$. Therefore, the hydrolytic rate sequence and the inertness of I to added nucleophiles strongly indicates an ionization mechanism.

In our earlier studies of the mechanisms of hydrolysis of acyl chlorides, it was possible to prove that dimethylcarbamyl chloride[3] and dimethylsulfamyl chloride[1] underwent ionization by trapping the intermediate ions by added nucleophiles. In the present case no products could be isolated which resulted from the reaction of pyrrolidine or *m*-cresoxide ion with the phosphinyl ion. The significance of these contrasting results is not clear. A possible explanation is that the phosphinyl ion is nonlinear, unlike the dimethylcarbamyl and dimethylsulfamyl ions, and that this fact detracts from the resonance stabilization of the ion.

The energy and entropy of activation for the hydrolysis of the alkoxy and dimethylamino derivatives of carbonyl, sulfonyl, and phosphinyl chlorides are presented for comparison in Table II.[4]

Acknowledgments. We are indebted to the Victor Chemical Works for a sample of I, to Dr. P. W. Morgan for helpful advice, and to Mr. Donald G. Preis for excellent technical assistance.

EXPERIMENTAL

Materials and methods. A sample of N,N,N^1,N^1-tetramethylphosphorodiamidic chloride was very kindly furnished by the Victor Chemical Works. It was a water-white liquid, n_D^{30} 1.4625. It contained a very slight deposit of crystalline material. Since we were unable to find published physical properties for this substance, it was analyzed.

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[1] Part II, *J. Am. Chem. Soc.*, in press.

[2] Dostrovsky and Halmann, *J. Chem. Soc.*, 502 *et seq.* (1953).

[3] Part I, Hall, Jr., *J. Am. Chem. Soc.*, **77**, 5993 (1955).

[4] A referee has been kind enough to point out that a plot of $\Delta E\ddagger$ *vs.* $\Delta S\ddagger$ is linear for the halides which undergo ionization. The rate constants for these halides are all quite similar in magnitude, however, and this fact may detract from the significance of the relationship.