

mixture of the two components only a color change was evident, but no reaction had taken place. Glpc analysis (4 ft \times 1/4 in, 20% Apiezon L on Chromosorb P column, 60–80 mesh) indicated that only starting materials were present. A few drops of tetrahydrofuran were added and a homogeneous solution resulted. This solution was heated on a steam bath overnight; glpc, however, indicated that no reaction had taken place.

Reaction of *cis*- and *trans*-Crotyltrimethylgermanium with Trifluoroacetic Acid.—In a flask equipped with a septum and a gas outlet to a Dry Ice–acetone trap was placed 0.141 g (8.2×10^{-4} mole) of *cis*- and *trans*-crotyltrimethylgermanium (60% *cis*, 40% *trans*). To this was added with a syringe 0.01 g (8.2×10^{-4} mole) of trifluoroacetic acid. The reaction was very exothermic, liberating a gas which was collected in the trap. Glpc analysis (15 ft 28% dimethylsulfolane on C-22 firebrick column, 40–60 mesh, at room temperature) indicated the presence of 1-butene, whose retention time was identical with that of an authentic sample and different from those of the isomeric 2-butenes.

Reaction of Cyclooct-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid.—In a flask equipped with a serum cap was placed 0.716 g (3.16×10^{-3} mole) of cyclooct-2-en-1-yltrimethylgermanium. To this was added 0.36 g (3.16×10^{-3} mole) of trifluoroacetic acid with a syringe. The reaction was very exothermic and was over in less than 1 min. Water and pentane were added and the pentane layer was separated, dried, and analyzed by glpc (4 ft, 20% Carbowax 20 M on Chromosorb P column, 40–60 mesh, isothermally at 75°, flow rate 20 cc/min). The glpc indicated that all the starting material was gone and that two products were present. The products were collected (glpc); the first peak was trimethylgermanium trifluoroacetate; the second was cyclooctene. The cyclooctene had an infrared spectrum which was superimposable on that of an authentic sample. Trimethylgermanium trifluoroacetate, n_D^{20} 1.3820, provided the following infrared spectral data: ν_{\max} (film) 2985 (m), 2900 (m), 1750 (s), 1400 (s), 1245 (m), 1210 (s), 1170 (s), and 835 (s) cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{14}\text{F}_3\text{GeO}_2$: C, 26.02; H, 3.90; F, 24.72. Found: C, 25.81; H, 4.15; F, 24.48.

Reaction of Cyclohex-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid.—To 0.2901 g (1.46×10^{-3} mole) of cyclohex-2-en-1-yltrimethylgermanium was added with a syringe 0.168 g (1.4×10^{-3} mole) of trifluoroacetic acid. An exothermic reaction commenced and was over in less than 1 min. Water and pentane were added, and the pentane layer was separated and dried over magnesium sulfate. Glpc analysis (4 ft, 20% Apiezon L on Chromosorb P column, 60–80 mesh, 100–220°, program 13°/min) indicated the presence of two peaks. The first peak was trimethylgermanium trifluoroacetate identified by infrared spectrum. The second was cyclohexene, identified by comparison of its retention time and infrared spectrum with those of an authentic sample. The starting material had completely reacted (glpc).

Reaction of Cyclopentadiene-Trimethylgermanium Hydride Adducts with Trifluoroacetic Acid.—To 0.1 g (6.7×10^{-4} mole) of cyclopentadienyltrimethylgermanium hydride adducts (62.7% 5, 37.3% 6) was added 0.07 g (6.7×10^{-4} mole) of trifluoroacetic acid dropwise from a syringe. The reaction mixture was analyzed by glpc (20 ft \times 3/8 in, 20% silicone nitrile on Chromosorb P column, 60–80 mesh, isothermally at 135°, flow rate 200 cc/min), showing that 6 reacted preferentially with the trifluoroacetic acid. The cyclopentene which was formed had a retention time (glpc) which was identical with that of an authentic sample.

Hydrogenation of the Trimethylgermanium Hydride-Bicyclo[2.2.1]heptadiene-2,5 Adducts.—To 0.70 g of the trimethylgermanium hydride-bicyclo[2.2.1]heptadiene-2,5 adducts (10, 11, and 12) dissolved in 5 ml of ethyl acetate was added 0.1 g of Adams catalyst. The mixture was hydrogenated at 25 psi in a Parr hydrogenator for 15 hr. The ethyl acetate was removed and the infrared spectrum indicated the absence of unsaturation. The nmr spectrum had trimethylgermanium singlets at τ 9.89 and 9.94 in the ratio 85:15, n_D^{25} 1.4813; infrared spectrum showed ν_{\max} 2960 (s), 1460 (m), 1250 (s), 1175 (w), 920 (w), 875 (w), and 840 (s) cm^{-1} ; nmr spectrum gave (neat) τ 7.7 (m), 8.7 (m), 9.89 (1), and 9.94 (1).

Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{Ge}$: C, 56.40; H, 9.40. Found: C, 56.67; H, 9.61.

Reactions of Phosphorus Compounds. XIII. Kinetics and Mechanism of the Reaction of Triphenylphosphine with α,α -Dihaloamides

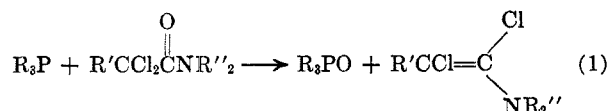
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The reaction of triphenylphosphine and α,α -dichloro- α -phenyl-N-methylacetanilide is a second-order polar reaction which is strongly accelerated by electron-withdrawing substituents attached to the α -phenyl group ($\rho = +2.6$). The results are consistent with a proposed mechanism involving initial attack of phosphorus on chlorine, and appear to rule out alternative mechanisms involving initial attack of phosphorus at the carbonyl oxygen, carbonyl carbon, or α carbon.

The reaction of trialkyl phosphites and trialkyl- or triarylphosphines with trichloroacetamides was shown to yield trichlorovinylamines.¹ The over-all transformation entailed the oxidation of a triply connected phosphorus compound with concomitant migration of a chlorine atom.



R = alkoxy, alkyl, aryl
R' = H, Cl, F, aryl
R'' = alkyl or aryl

With the data available at that time on this and the Perkow reactions,² a rational mechanistic explanation

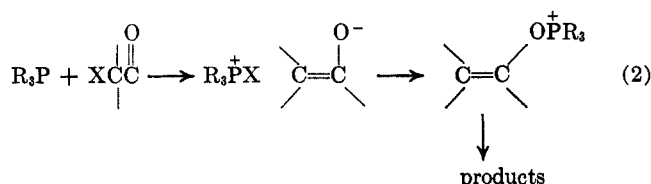
which depicted these reactions to proceed *via* attack of phosphorus on the carbonyl oxygen atom of the amide rather than the carbonyl carbon or α -carbon atom was postulated.

In order to elucidate the point of attack of the phosphine on the amide, the reaction of tertiary phosphines with α -substituted dichloroacetamides was studied. N,N-Diethyl- α,α -dichloro- α -fluoroacetamide with tributylphosphine gave a very low yield of α,β -dichloro- β -fluorovinylamine (13% at 125–130°), whereas N,N-diethyltrichloroacetamide in the same reaction gave a 74% yield of the trichloroamine at room temperature. This striking difference in reactivity is inconsistent with attack at either the carbonyl carbon or carbonyl oxygen atoms, but strongly favors initial attack by phosphorus on the α -chlorine atom.³ The reaction of

(1) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 903 (1960).
(2) W. Perkow, *Chem. Ber.*, **87**, 755 (1954); W. Perkow, E. W. Krockow, and K. Knoevenagel, *ibid.*, **88**, 662 (1955).

(3) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962).

tertiary phosphorus compounds with α -halocarbonyl compounds was formulated as shown in eq 2.



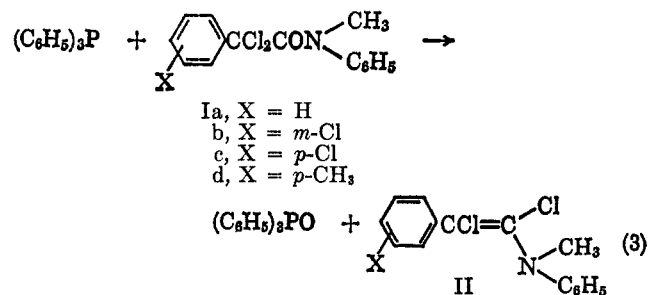
The reactions of trivalent phosphorus compounds with N-haloamides, α -bromonitroalkanes, and bromoacetonitrile and in the Perkow reaction were also postulated to involve the initial attack of phosphorus on halogen.³

Additional qualitative evidence for initial nucleophilic attack of phosphorus on halogen was supplied by several other investigators.⁴

In certain other reactions it has been possible to demonstrate that a compound containing a phosphorus-halogen bond is formed. Treatment of α,β -dibromoamides and esters with triphenylphosphine affords triphenylphosphine dibromide and the α,β -unsaturated amide or ester.⁵ The reaction of trialkylphosphates and hexachlorocyclopentadiene almost certainly proceeds *via* a chlorophosphonium-cyclopentadienide ion pair.⁶ In the reaction of trimethyl phosphite and 4-bromocyclohexadienones bearing bulky groups in the 2 and 6 positions,⁷ the formation of dimethylphosphorobromidate and the lack of observable steric retardations strongly support a "halogen attack" mechanism.

Stable enol phosphonium salts have been obtained from reactions of triphenylphosphine and suitably substituted α -haloacetophenones. The ease of formation of the salts is clearly related to the ability of substituents to stabilize the enolate ion.^{8,9} Furthermore, pyrolysis of the salts has been shown to lead to replacement of the phosphine oxide grouping by halogen. Clearly, then, precedents do exist for each step in the proposed mechanism 2.

In spite of the wealth of evidence which favors the "halogen attack" mechanism, a detailed kinetic study has not been made. We have undertaken such a study of the reactions of triphenylphosphine with substituted α,α -dichloro- α -phenylamides (I) (see eq 3 following).



Ia, X = H
b, X = *m*-Cl
c, X = *p*-Cl
d, X = *p*-CH₃

(4) For recent reviews, see H. Hoffmann and H. J. Diehr, *Angew. Chem. Intern. Ed. Engl.*, **3**, 737 (1964); B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, pp 133-199.

(5) C. C. Tung and A. J. Speziale, *J. Org. Chem.*, **28**, 1521 (1963).

(6) V. Mark, *Tetrahedron Letters*, No. 9, 295 (1961).

(7) B. Miller, *J. Org. Chem.*, **30**, 1964 (1965).

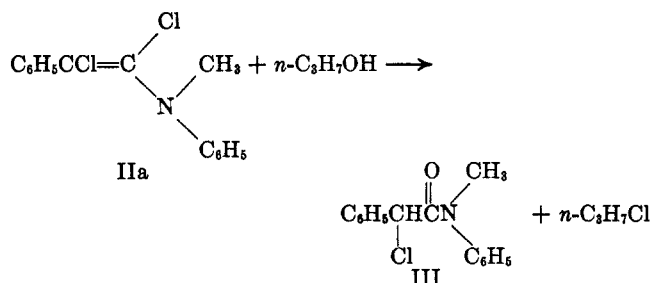
(8) R. D. Partos and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 5068 (1965).

(9) A. J. Speziale, R. D. Partos, and L. J. Taylor, "Reaction of Trivalent Phosphorus with Halocarbonyl Compounds," IUPAC International Symposium on Organophosphorus Compounds, Heidelberg, Germany, May 20-24, 1964.

If a carbanion were formed by rate-determining attack of phosphorus on chlorine, the reaction should be facilitated by electron-withdrawing substituents and a large positive Hammett ρ value would be expected. The reaction might be accelerated by electron-withdrawing substituents even if attack of phosphorus occurs at another atom (*e.g.*, the oxygen, α carbon, or carbonyl carbon),¹⁰ but the effect should then be considerably smaller, since the rate-determining step would not involve the formation of a benzylic anion.

Results

In order to establish that the reactions proceed in the expected manner (eq 3) under conditions similar to those employed in kinetic studies, the products of the reaction of triphenylphosphine and amide Ia in acetonitrile were characterized. Crude N-methyl-N-phenyl- α,β -dichloro- β -styrylamine (IIa, *cis*, *trans*, or mixture) and crude triphenylphosphine oxide were isolated in 95 and 90% yield, respectively. The styrylamine IIa was characterized by microanalysis and by its infrared, ultraviolet, nuclear magnetic resonance, and mass spectra. Furthermore, treatment of IIa with *n*-propyl alcohol afforded *n*-propyl chloride and α -chloro- α -phenyl-N-methylacetanilide (III), in accordance with the known¹¹ reaction of alcohols with chloroenamines.



A series of preliminary kinetic runs were conducted in which the initial concentrations of triphenylphosphine and amide Ia were varied. The results (Table I) clearly demonstrate that the reaction 3 is second order, first order with respect to each reactant.

TABLE I
OBSERVED SECOND-ORDER RATE CONSTANTS FOR
REACTION OF TRIPHENYLPHOSPHINE AND AMIDE Ia
IN ACETONITRILE AT $59.7 \pm 0.1^\circ$

Initial concn, ^a M		$k_2 \times 10^4, M^{-1} \text{sec}^{-1b}$
Phosphine	Amide	
0.0469	0.1417	7.6 ± 0.8
0.1438	0.0473	7.9 ± 0.6
0.1426	0.0944	7.9 ± 0.6
0.1137	0.1140	7.3 ± 0.6
0.1427	0.1425	6.9 ± 1.0

^a Concentrations corrected for thermal expansion of solvent.

^b In this and succeeding tables, k_2 denotes the observed second-order rate constant for the over-all reaction.

(10) For a recent discussion of various possible mechanisms of the Perkow reaction, see P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, **21**, 1961 (1965). The reaction of trialkylphosphites and certain, simple α -monohaloketones may indeed proceed by initial attack of phosphorus at carbonyl carbon, as these authors suggest. However, the attack of triphenylphosphine at the carbonyl carbon atom of α,α,α -trichloro- and α,α -dichloro- α -phenylamides would be subject to severe steric hindrance. For this reason, as well as the previously cited difference in reactivity of trichloro- and α -fluorodichloroamides and the substituent effects described below, we believe a mechanism involving initial attack of phosphorus on carbonyl carbon would be very unlikely in the present instance.

(11) A. J. Speziale and R. C. Freeman, *J. Am. Chem. Soc.*, **82**, 909 (1960).

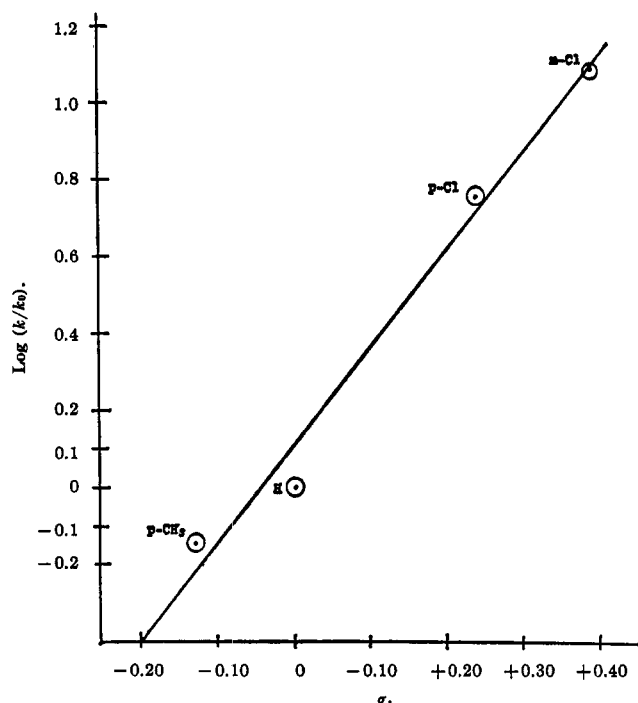


Figure 1.—Hammett plot, reactions of triphenylphosphine and amides Ia-d, in acetonitrile at $59.7 \pm 0.1^\circ$.

An investigation of solvent effects showed that, as expected, the reaction proceeds more rapidly in more polar solvents (Table II).

TABLE II
SOLVENT EFFECTS ON REACTION OF
TRIPHENYLPHOSPHINE AND AMIDE Ib
AT $59.7 \pm 0.1^\circ$ ^a

Solvent	Dielectric constant ^b	$k_2 \times 10^5$, $M^{-1} \text{sec}^{-1}$	Rel k
Acetonitrile	37.5 (20)	95.7 ± 1.0	5.7
Butyronitrile	20.3 (21)	46.4 ± 3.1	2.8
Chlorobenzene	5.6 (25)	32.5 ± 0.9	1.9
Benzene	2.3 (20)	16.8 ± 1.0	1.0

^a Initial concentrations approximately 0.15 M phosphine, 0.10 M amide. ^b Dielectric constants taken from "Technique of Organic Chemistry," Vol. VII, A. Weissberger, Ed., 2nd ed, Interscience Publishers, Inc. New York, N. Y., 1955, pp 270-274.

The more nucleophilic *n*-butyldiphenylphosphine reacts with amide Ia about 8.4 times faster than triphenylphosphine ($k_2 = 66.1 \pm 3.0 \times 10^{-5} M^{-1} \text{sec}^{-1}$ and $7.87 \pm 0.02 \times 10^{-5} M^{-1} \text{sec}^{-1}$, respectively, in acetonitrile at $59.7 \pm 0.1^\circ$).

The reaction of triphenylphosphine and the *m*-chloroamide Ib in acetonitrile was found to proceed 5.1 times as rapidly at 59.7° as at 40.1° ($k_2 = 18.6 \pm 1.6 \times 10^{-5} M^{-1} \text{sec}^{-1}$). Calculation of the activation parameters gives $\Delta H^\ddagger = 15.7 \text{ kcal/mole}$, $\Delta S^\ddagger = -25.5 \text{ eu}$.¹²

The possibility of a free-radical reaction was eliminated by demonstrating that addition of a free-radical initiator (azobisisobutyronitrile, $k_2 = 7.8 \pm 0.5 \times 10^{-5} M^{-1} \text{sec}^{-1}$) or an inhibitor (2,5-di-*t*-butylhydroquinone, $k_2 = 7.5 \pm 0.4 \times 10^{-5} M^{-1} \text{sec}^{-1}$) had no effect on the rate of reaction in acetonitrile at $59.7 \pm 0.1^\circ$.

Rate constant for reactions of triphenylphosphine with the substituted amide are given in Table III.

(12) These values are based on a single kinetic run at one lower temperature and should be regarded as approximate.

TABLE III

RATE CONSTANTS FOR REACTION OF TRIPHENYLPHOSPHINE AND SUBSTITUTED AMIDES OF TYPE $\text{XC}_6\text{H}_4\text{CCl}_2\text{CON}(\text{CH}_2)_6\text{C}_6\text{H}_5$ IN ACETONITRILE AT $59.7 \pm 0.1^\circ$ ^a

Amide	X	$k_2 \times 10^5$, $M^{-1} \text{sec}^{-1}$	Rel k
Ib	<i>m</i> -Cl	95.7 ± 1.0	12.16
Ic	<i>p</i> -Cl	44.7 ± 0.8	5.68
Ia	H	7.87 ± 0.02	1.00
Id	<i>p</i> -CH ₃	5.66 ± 0.13	0.72

^a Initial concentrations approximately 0.15 M phosphine, 0.10 M amide.

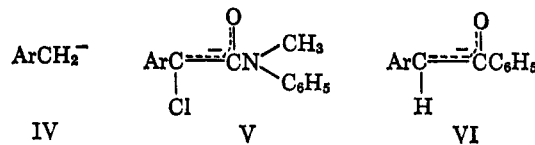
A Hammett plot of the data is shown in Figure 1. σ values were taken from the tabulation of Bekkum, Verkade, and Wepster.¹³ Calculation of the slope by the method of least squares¹⁴ gives $\rho = +2.58$, with a correlation coefficient (r) of 0.993.

One might expect to obtain an improved correlation by using the ionization of phenols as a model of a reaction in which a negative charge is formed on an atom adjacent to the aromatic ring. In fact, this appears to be the case. Use of σ values calculated¹⁵ from the ionization constants of phenols in 95% ethyl alcohol gives $\rho = 2.65$, $r = 0.996$. Use of σ values calculated¹⁵ from ionization of phenols in 8% dioxane gives $\rho = +2.81$, $r = 0.995$.

Discussion of Results

The ρ value of +2.6 obtained in the present work is close to the ρ value (+2.75) found¹⁵ in ethoxide-catalyzed E2 elimination reactions of β -arylethylsulfonium ions at 30° and to ρ (+2.8) observed¹⁶ in *t*-butoxide-catalyzed *cis*-eliminations from 2-arylcyclopentyl tosylates at 50° . In both of these reactions the carbanionic character of the transition state is believed¹⁵⁻¹⁷ to be relatively high.

Furthermore, a value of +2.6 is intermediate between the value of +4.0 found for lithium cyclohexylamide-catalyzed hydrogen exchange¹⁸ of substituted toluenes at 50° and that (+1.73) observed in acetate-catalyzed bromination¹⁹ of benzyl phenyl ketones at 25° . This comparison seems entirely reasonable, since a benzylic carbanion V formed by attack of phosphorus on chlorine should be intermediate in stability between a benzylic anion IV and the enolate, anion of a



benzyl phenyl ketone VI. Consequently, a reaction proceeding *via* anion V might be expected to be less sensitive to substituents than one proceeding *via* IV, but more sensitive than one involving anion VI.

(13) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

(14) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

(15) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957).

(16) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *ibid.*, **87**, 2421 (1965).

(17) J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962).

(18) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964).

(19) A. Fischer, J. Packer, and J. Vaughan, *J. Chem. Soc.*, 226 (1963).

Clearly, then, the observed ρ value is consistent with the "halogen attack" mechanism; it is also too large to be easily rationalized in terms of most alternative mechanisms.²⁰ For example, a reaction proceeding by initial attack of phosphorus on carbonyl carbon should exhibit much smaller substituent effects, since the aromatic ring would be insulated from the reaction center by the dichloromethylene group (*cf.* $\rho = 0.97$ at 25° for alkaline hydrolysis of ethyl phenylacetates).²¹

Attack of phosphorus on the α carbon, with S_N2 displacement of chloride ion, might be weakly accelerated by electron-withdrawing substituents (*cf.* $\rho = 0.79$ in reaction of benzyl chlorides with potassium iodide in acetone),¹⁴ but one would hardly expect an effect as large as that observed.

Similarly, one would not expect a large ρ value in the case of initial attack on oxygen, with S_N2' -type displacement of chloride; the α -carbon atom does not bear a negative charge in the resulting intermediate (enol phosphonium salt).

We conclude that the present results strongly support the "halogen attack" mechanism.²²

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Beckman IR-5A. Nmr spectra were obtained on a Varian A-60, with tetramethylsilane as internal reference. Ultraviolet spectra were obtained on a Beckman DK-2A. A Consolidated Electrodynamics Model 21-103C was employed for mass spectral analyses.

Unless otherwise specified, commercially available reagents were used without further purification. Solvents were dried over Molecular Sieve 4A.

For use in kinetic experiments, butyronitrile, chlorobenzene, and benzene were subjected to preliminary drying over anhydrous calcium chloride, then fractionally distilled from calcium hydride.

Reagent grade triphenylphosphine (J. T. Baker) was recrystallized four times from absolute ethyl alcohol. The recrystallized material was powdered and dried in a vacuum desiccator to give white crystals, mp 80–81°.

Commercial acetonitrile (Fisher reagent) was dried by stirring with calcium hydride, distilled from phosphorus pentoxide, and redistilled from calcium hydride.²³ The purified material, bp 87°, was stored over Molecular Sieve 4A in a glass-stoppered bottle of "low actinic" glass. Karl Fisher titration showed the water content of the purified acetonitrile to be 0.01% or less.

***n*-Butyldiphenylphosphine.**—*n*-Butylmagnesium bromide was prepared under nitrogen from *n*-butylbromide (80 g, 0.56 mole) and magnesium (15 g, 0.60 mole) in ether. An ether solution of chlorodiphenylphosphine (100 g, 0.45 mole) was added dropwise, and the mixture was refluxed for 2 hr. It was then treated with a solution of 30 g of ammonium chloride in 200 ml of water and filtered; the ether layer was separated and dried over anhydrous magnesium sulfate. Evaporation of the ether followed by vacuum distillation gave *n*-butyldiphenylphosphine (96 g, 88%) as a clear colorless liquid, bp 128–130° (0.8 mm) [lit.²⁴ bp 117–120° (0.3 mm)].

α,α -Dichloro- α -phenyl-*N*-methylacetanilide (Ia).—A round-bottom flask fitted with a thermometer and an 8-in. Vigreux distilling column was charged with 208.3 g (1.0 mole) of phosphorus pentachloride and 77.3 g (0.5 mole) of phenylacetyl chloride. The apparatus was protected by a drying tube. The

mixture was refluxed 1 hr (150–200°) during which time 102.5 g (0.75 mole, 75%) of phosphorus trichloride, bp 66–72°, was distilled. Vacuum distillation of the residue gave 2,2-dichlorophenylacetyl chloride as a colorless liquid (80.7 g, 0.36 mole, 72%), bp 75–80° (0.9 mm), n_D^{20} 1.5500 (lit.³ n_D^{20} 1.5490).

An ice-cold solution of 76.5 g (0.714 mole) *N*-methylaniline in 400 ml of anhydrous ether was added to an ice-cold solution of 79.8 g (0.357 mole) of the acid chloride in 400 ml of anhydrous ether. The precipitate was filtered and the filtrate was stirred 24 hr at room temperature in a nitrogen atmosphere. The solution was filtered again and the filtrate was extracted with two 400-ml portions of 6 *M* hydrochloric acid, followed by two of 10% sodium carbonate, and one of saturated sodium chloride, and dried over anhydrous sodium sulfate. Evaporation of the ether gave 84.5 g (81%) of light yellow solid. Its infrared spectrum ($CHCl_3$) contained a carbonyl band at 6.0 μ , while its nmr spectrum ($CDCl_3$) showed an aromatic multiplet (τ 2.5–3.3) and *N*-methyl singlet at τ 6.75 (relative areas 3.5:1). Four recrystallizations from methylcyclohexane yielded white crystals, mp 66.5–67.5°.

Anal. Calcd for $C_{15}H_{13}Cl_2NO$: C, 61.24; H, 4.45; Cl, 24.11. Found: C, 61.19; H, 4.38; Cl, 24.02.

α,α -Dichloro- α -(*m*-chlorophenyl)-*N*-methylacetanilide (Ib).—A round-bottom flask fitted with a thermometer and an 8-in. Vigreux distilling column was charged with 187.5 g (0.90 mole) of phosphorus pentachloride and 48.6 g (0.285 mole) of *m*-chlorophenylacetic acid. The apparatus was protected by a drying tube and the mixture was refluxed 4.5 hr (130–160°) during which 86 g (0.6 mole, 100%) of phosphorus trichloride, bp 68–77°, was distilled. A water pump was attached and phosphorus oxychloride was removed by warming to 140° (15 mm). The residue consisted of 67 g (0.26 mole, 91%) of crude acid chloride (clear yellow liquid).

An ice-cold solution of 56 g (0.52 mole) of *N*-methylaniline in 300 ml of anhydrous ether was added to a solution of the crude acid chloride (67 g, 0.26 mole) in 300 ml of anhydrous ether. The mixture was stirred 24 hr at room temperature in a nitrogen atmosphere and filtered. The filtrate was extracted with two 300-ml portions of 6 *M* hydrochloric acid, two of 10% sodium carbonate, and one of saturated sodium chloride, and then dried over anhydrous sodium sulfate, and evaporated. This gave 74.5 g (79% over-all yield) of a yellow solid; its infrared spectrum ($CHCl_3$) contained an amide band at 6.0 μ , while its nmr spectrum (CCl_4) exhibited an aromatic multiplet at τ 2.8–3.5 and a methyl singlet at 6.8 μ (relative areas 3:1). One recrystallization from methylcyclohexane, followed by two recrystallizations from ethyl acetate, yielded white crystals, mp 91–92°.

Anal. Calcd for $C_{15}H_{12}Cl_2NO$: C, 54.82; H, 3.68; Cl, 32.37. Found: C, 54.78; H, 3.75; Cl, 32.40.

α,α -Dichloro- α -(*p*-chlorophenyl)-*N*-methylacetanilide (Ic).— α,α -Dichloro-*p*-chlorophenylacetyl chloride was similarly prepared from phosphorus pentachloride and *p*-chlorophenylacetic acid. Treatment with 2 equiv of *N*-methylaniline in ether yielded the amide in 72% over-all yield. Charcoal decolorization of the crude amide followed by five recrystallizations from methylcyclohexane yielded white crystals, mp 86–87°.

Anal. Calcd for $C_{15}H_{12}Cl_2NO$: C, 54.82; H, 3.68; Cl, 32.37. Found: C, 54.67; H, 3.72; Cl, 32.27.

***p*-Tolylglyoxylic Acid.**—A three-necked flask fitted with mechanical stirrer was charged with 117.5 g (0.74 mole) of potassium permanganate, 3500 ml of distilled water, and 250 ml of 10% sodium hydroxide. The mixture was cooled to 10°, and 50 g (0.37 mole) of *p*-methylacetophenone was added. The reaction mixture was stirred 2 hr at 5–10° and filtered. The filtrate was acidified with 250 ml of 6 *M* hydrochloric acid, and extracted with two 1200-ml portions of ether, which were combined and extracted with two 1000-ml portions of 5% sodium bicarbonate. The bicarbonate extracts were acidified with 300 ml of 6 *M* hydrochloric acid, and extracted with two 600-ml portions of ether. The ether solution was washed with saturated sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated.

The residue (61 g, white oil) was suspended in benzene and water was removed azeotropically (Dean–Stark trap). A white solid crystallized from benzene, 18.1 g, mp 90–96° (lit.²⁵ mp 97°). Concentration of the mother liquor afforded a second crop of 13.1 g of white crystals, mp 84–92° (combined yield

(20) The following arguments implicitly assume that the initial step of alternative multistep mechanisms is rate determining. However, similar arguments can be advanced, even if the decomposition or rearrangement of an intermediate phosphonium salt is rate determining.

(21) R. O. C. Norman and P. D. Ralph, *J. Chem. Soc.*, 5431 (1963).

(22) Of course, the present results give no information about mechanistic steps which may follow the rate-determining one. Discussions of evidence concerning the intermediacy of enol phosphonium salts and the mechanism of their decomposition to products may be found in ref 3 and 8.

(23) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

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(25) L. Bouveault, *Bull. Soc. Chim. France*, **17**, 363 (1897).

31.2 g, 51%). The product was identified as *p*-tolylglyoxylic acid by comparison of its infrared and nmr spectra with those of a sample prepared by Friedel-Crafts reaction of toluene and ethyl oxalyl chloride, followed by hydrolysis of the resulting ester.²⁷

α,α -Dichloro- α -(*p*-tolyl)-*N*-methylacetanilide (Id).—A four-necked flask fitted with thermometer, reflux condenser, and magnetic stirrer was flushed with dry nitrogen and charged with 31.2 g (0.19 mole) of *p*-tolylglyoxylic acid, 87.0 g (0.42 mole) of phosphorus pentachloride, and 75 ml of ethylene chloride. An atmosphere of dry nitrogen was maintained while the mixture was stirred for 1 hr at room temperature, then refluxed for 10.5 hr (91–92°). Ethylene chloride and phosphorus oxychloride were removed by warming to 55° (20 mm). The residue, filtered to remove unreacted phosphorus pentachloride, yielded the α,α -dichloro acid chloride as a clear yellow liquid (39.7 g, 88%).

An ice-cold solution of 42.9 g (0.40 mole) *N*-methylaniline in 200 ml of anhydrous ether was added to an ice-cold solution of 39.7 g (0.17 mole) of the acid chloride in 200 ml of anhydrous ether. The white precipitate was filtered and the filtrate was stirred for 24 hr at room temperature under a nitrogen atmosphere. The reaction mixture was filtered again and the filtrate was washed with two 500-ml portions of 6 *M* hydrochloric acid, followed by two of 10% sodium carbonate and one of saturated sodium chloride, dried over anhydrous sodium sulfate, and evaporated. This gave 40.3 g of tan semisolid (over-all 69% yield of crude product); its infrared spectrum (CHCl₃) contained an amide band at 6.0 μ , while its nmr spectrum (CDCl₃) consisted of an aromatic multiplet at τ 2.8–3.4, a singlet (*N*-methyl) at τ 6.9, and a singlet (*p*-methyl) at τ 7.7 (relative areas 3.9:1:1). One recrystallization from *n*-hexane, followed by four recrystallizations from methylcyclohexane, yielded white crystals, mp 81.0–82.5°.

Anal. Calcd for C₁₆H₁₅Cl₂NO: C, 62.35; H, 4.91; Cl, 23.01. Found: C, 62.31; H, 4.86; Cl, 22.97.

Characterization of Reaction Products.—A solution of 26.2 g (0.10 mole) of triphenylphosphine and 29.4 g (0.10 mole) of α,α -dichloro- α -phenyl-*N*-methylacetanilide (Ia) in 175 ml of anhydrous acetonitrile was refluxed for 48 hr in an atmosphere of dry nitrogen. Acetonitrile was then evaporated. Short-path distillation of the residue gave 26.5 g (95%) of crude *N*-methyl-*N*-phenyl- α,β -dichloro- β -styrylamine (IIa) as a yellow liquid, bp 164–172° (0.7–1.2 mm). The tan solid residue, mp 147–153°, whose infrared and nmr spectra indicated it to be nearly pure triphenylphosphine oxide (25.0 g, 90% yield), was crystallized from acetonitrile and gave 12.4 g of triphenylphosphine oxide, mp 151–157° (no depression of mixture melting point); concentration of the mother liquor afforded a second crop of 5.1 g, mp 148–153°.

Redistillation of a portion of the crude styrylamine through a 45 × 0.5 cm spinning-band column gave as the center fraction a clear light yellow liquid, bp 96–99° (0.08–0.09 mm).

Anal. Calcd for C₁₅H₁₃Cl₂N: C, 64.75; H, 4.71; Cl, 25.49; N, 5.04. Found: C, 64.85; H, 4.80; Cl, 25.42; N, 5.09.

The infrared spectrum (CCl₄) of the styrylamine showed no appreciable absorption in the carbonyl region, but a strong band was present at 6.25 μ (conjugated C=C). The nmr spectrum (CCl₄) contained two multiplets in the aromatic region (τ 2.5–2.9 and τ 3.0–3.3, relative areas 9.9 and 4.2 units) and singlets at τ 6.8 and 7.1 (relative areas 1.0 and 3.2 units). The two singlets are tentatively assigned to *N*-methyl groups of *cis* and *trans* isomers, although the possibility that two *N*-methyl peaks might arise from restricted rotation is also recognized.

The ultraviolet spectrum (CH₃CN) of the styrylamine contained a maximum at 240 $m\mu$ (ϵ 16,000) and a shoulder at 290 $m\mu$ (ϵ 4000). Its mass spectrum contained the expected molecular ion peak at *m/e* 277 (accompanied by ³⁷Cl isotope peaks at *m/e* 279 and 281) and large fragment peaks at *m/e* 242 (loss of one chlorine atom) and *m/e* 207 (loss of both chlorine atoms), the latter being the base peak. The peak at *m/e* 277 was the largest peak in the low-voltage mass spectrum.

Reaction of *N*-Methyl-*N*-phenyl- α,β -dichloro- β -styrylamine and *n*-Propyl Alcohol.—A round-bottom flask was charged with 14.3 g (0.051 mole) of the styrylamine and 50 ml of *n*-propyl alcohol. A 6-in. Vigreux distilling column was attached and the mixture was refluxed 1.5 hr. During this period 2.4 g (59%) of *n*-propyl chloride, bp 46–50°, was distilled. The identity of the

n-propyl chloride was confirmed by nmr spectroscopy and by gas chromatography.

Removal of the excess *n*-propyl alcohol (vacuum pump) gave a residue of 13.1 g (98%) of a light brown oil, which solidified on standing. One recrystallization from ethyl alcohol–water, followed by another from methylcyclohexane, yielded 6.2 g of α -chloro- α -phenyl-*N*-methylacetanilide (white crystals, mp 61.5–63.5°), which was identical (infrared spectra, mixture melting point) with an authentic sample prepared from α -chlorophenylacetyl chloride and *N*-methylaniline.

Analytical Method.—The disappearance of phosphine was followed by an iodimetric titration method similar to that previously employed^{26,27} for kinetic studies of reactions of triphenylphosphine. In the present instance the end point was improved by adding a cosolvent (acetic acid) which would permit the titration of iodine with thiosulfate and the use of starch as indicator.²⁸ Preliminary experiments demonstrated that the other reactants and products would not interfere with the titration. Furthermore, it was shown that values of the “per cent reaction” obtained by this method agreed very well with those determined by infrared analysis.

Each 5-ml aliquot of a solution 0.00–0.15 *M* in triphenylphosphine was added to a mixture of 10.0 ml of 0.1 *M* aqueous iodine (containing excess potassium iodide) and 50 ml of glacial acetic acid. The resulting mixture was agitated with a magnetic stirrer and titrated with 0.1 *M* aqueous sodium thiosulfate. About 5 ml of 0.2% starch solution was added near the end point. By comparing the titers obtained with and without acetic acid and the reaction solvent added to the iodine solution, a correction (typically 0.3 ml, 0.1 *M* thiosulfate) was applied for the “indicator blank.”

Kinetic Procedure.—Appropriate quantities of phosphine and amide were weighed into a volumetric flask, which was then placed in a glove bag filled with dry nitrogen. The reaction mixture was prepared and transferred to an erlenmeyer flask with a standard-taper joint and a side arm bearing a Teflon stopcock. The joint was closed by a solid Teflon stopper, the reaction flask was removed from the glove bag, the side arm was connected to a stream of dry nitrogen flowing to a bubble tube, and the reaction flask was clamped in a constant temperature bath. The stopcock was opened to permit pressure equilibration as the reaction mixture was warmed to the bath temperature, and to allow a slow stream of nitrogen to sweep out the neck of the flask during sampling. The reaction mixture was sampled, at intervals corresponding to about 20–80% reaction, with a pipet calibrated for delivery of the proper solvent at the reaction temperature. Control experiments showed that evaporation of solvent could be neglected. A standard solution of triphenylphosphine in acetonitrile, prepared and sampled in this manner, showed no appreciable change in concentration over a 5-day period at 60°. Addition of Molecular Sieve 4A to a reaction mixture produced no change in the observed rate; this suggests that the moisture content of the reaction mixtures (0.00–0.10% by Karl Fisher titration) was too low to affect the kinetics.

Calculation of Rate Constants.—For each kinetic point, the corresponding concentrations of phosphine and amide were calculated; small corrections were applied for the “indicator blank” and for the thermal expansion of the solvent. The rate constant was then obtained from the slope of the appropriate second-order plot. For single kinetic runs the uncertainty in the observed rate constant was estimated by calculating a “rate constant” corresponding to each point and computing the standard deviation of the mean. If two or more kinetic runs were performed under the same conditions, the observed rate constants were averaged and the uncertainty was taken as the standard deviation of their mean.

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(28) Acetic acid is employed as a cosolvent in the determination of iodine numbers. See, for example, S. Siggia, “Quantitative Organic Analysis via Functional Groups,” 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1963, pp 313–318.