Kinetics and Mechanism of the Reaction of Triphenylphosphine with α-Haloacetophenones[1]

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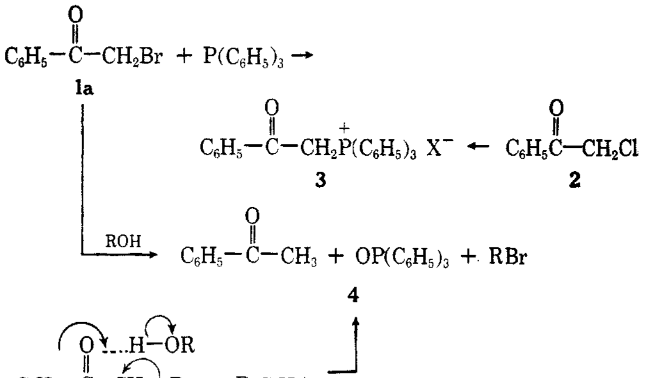
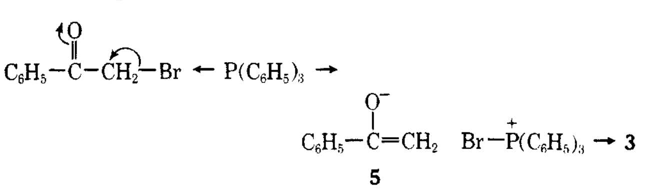
The reaction of triphenylphosphine and α-bromoacetophenone in nitromethane is a second-order reaction which is only weakly accelerated by electron-withdrawing substituents on the phenyl group ($\rho = +0.44$). Similar results are found for the reaction of pyridine with α-bromoacetophenone ($\rho = +0.30$) in nitromethane. The reactions of α-chloroacetophenone with triphenylphosphine or pyridine are much slower and also second order over-all. The simplest mechanism for all of these reactions involves an SN2 type of displacement of halide ion by the nucleophile. Attack on bromine of α-bromoacetophenone by triphenylphosphine, which gives the debrominated ketone, may occur only in the presence of prototropic species.

It is known that α-bromoacetophenone (**1a**) and α-chloroacetophenone (**2**) react with triphenylphosphine in aprotic solvents to give the corresponding ketophosphonium halide **3**.[3] In the presence of prototropic species, such as methanol or acetic acid, **1a** is debrominated by triphenylphosphine to give acetophenone (**4**) while **2** still gives the ketophosphonium chloride.

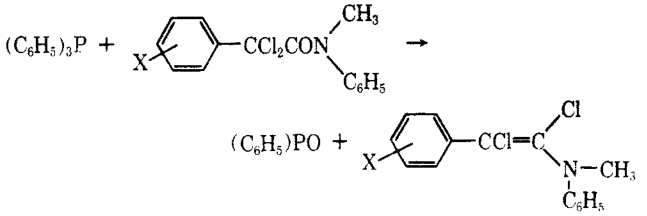
The debromination of α-bromo ketones with triphenylphosphine in the presence of prototropic species has been found to be general.[4] It has been postulated that the debrominations proceed *via* attack on bromine by triphenylphosphine in a concerted reaction involving prior or concurrent protonation of an incipient enolate ion by the prototropic species present.[4b]



It was further postulated that **2** always reacts with triphenylphosphine *via* simple displacement of chloride ion and never *via* attack on chlorine. This left open the question of how **1a** reacts with triphenylphosphine in aprotic solvents. The simplest pathway for the conversion of **1a** to **3** would, of course, involve simple displacement of bromide ion. A number of considerations,[5] however, led us to postulate initial attack on bromine to give an enolate bromotriphenylphosphonium ion pair **5** which could then give **3**.



In a number of α-haloacetophenones substituted by electron-withdrawing groups (such as phenyl or halogen) reaction with triphenylphosphine gives isolable enol phosphonium salts or products clearly derived from such species.[6] Attack on bromine by triphenylphosphine in such cases would lead to a stabilized enolate which then undergoes phosphonium salt formation at the less hindered oxygen site. The only kinetic study on such a system that has been reported to date was done by Speziale[7] on the α,α-dichloro-α-phenyl-N-methylacetanilide system in reaction with triphenylphosphine. A large Hammett ρ value (+2.6) was found, in good agreement with the "halogen attack" mechanism.



In order to establish whether **1a** reacts with triphenylphosphine in aprotic solvents *via* direct displacement of bromide ion or by rate-determining attack by phosphorus on bromine, a kinetic study of the reaction including the determination of the ρ value was made. Kinetic comparisons with the reactions of **1a** with pyridine and **2** with both pyridine and triphenylphosphine were made. The reactions of either **1a** or **2** with pyridine are well known to involve displacement of halide ion and to give small positive ρ values.

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(1) (a) This research was initiated at the Department of Chemistry, Lehigh University, Bethlehem, Pa. (b) Organophosphorus Chemistry, VI. (c) This investigation was supported by Grants AF-AFOSR 938-65 and 1170-66 from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(2) Belfer Graduate School of Science, Yeshiva University.

(3) (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (b) I. J. Borowtiz and L. I. Grossman, *Tetrahedron Letters*, 471 (1962); (c) H. Hoffman and H. J. Diehr, *ibid.*, No. 13, 583 (1962); (d) I. J. Borowitz and R. Virkhaus, *J. Am. Chem. Soc.*, **85**, 2183 (1963).

(4) (a) S. Trippett, *J. Chem. Soc.*, 2337 (1962); (b) I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

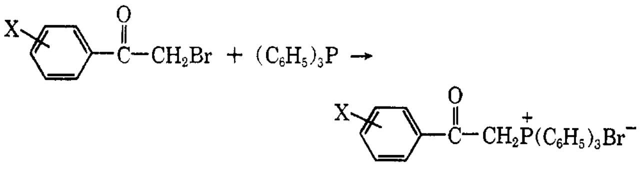
(5) *Cf.* (a) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2. M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1965; (b) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter 5.

(6) (a) R. D. Partos and A. J. Speziale, *J. Am. Chem. Soc.*, **87**, 5068 (1965); (b) *cf.* ref 3b, 3c, and 4b; (c) R. Virkhaus, Ph.D. Dissertation, Lehigh University, 1965; (d) P. Rusek and K. Kirby, research in progress.

(7) A. J. Speziale and L. J. Taylor, *J. Org. Chem.*, **31**, 2450 (1966).

Results

The reaction of triphenylphosphine with a series of phenyl-substituted bromoacetophenones in nitromethane were found to be second order over-all as followed by a standard conductometric method.[8a]



3a-3f

1a, X = H
b, X = p-CH$_3$O
c, X = p-CH$_3$
d, X = p-Br
e, X = p-NO$_2$
f, X = m-CH$_3$O

Thus an excellent linear plot of $R/R - R_\infty$ *vs.* time was obtained in each case. In addition, for the reaction of **1a** with triphenylphosphine, the reaction order was calculated from the equation[8b]

$$n = 1 + \frac{\log [(t_2/t_1) - 1]}{\log [1/(1 - y)]}$$

where n is the order of the reaction, t_1 was found to be 5.6 min, and t_2 was 12.8 min, for a chosen fraction of reaction, y, set at 0.2. In this expression $t_1 = a(1 - y)$ and $t_2 = a(1 - y)^2$. This gave $n = 2.10$ which is in good agreement with a second-order reaction.

In several cases it was shown that the reactants gave the desired ketophosphonium salts in high yield in nonkinetic runs. In the actual kinetic runs, examination (by tlc) of the reaction mixtures after completion of the conductometric readings showed that only the phosphonium salt was present. Furthermore, in the reaction of **1a** with triphenylphosphine, a calibration curve relating conductance readings to actual concentration was made for each cell used and it showed the kinetic runs to proceed to 97–98% of completion.

With further regard to the stoichiometry of the reactions, the initial concentration of **1a** and triphenylphosphine were varied. Table I indicates that the reaction of **1a** with triphenylphosphine is second order over-all and first order with respect to each reactant.

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF TRIPHENYLPHOSPHINE AND α-BROMOACETOPHENONE IN NITROMETHANE AT 34.90 ± 0.01°

Initial concn, M		k_2, l. mole^{-1} min^{-1}
Phosphine	Bromo ketone	
0.0100	0.0100	5.84 ± 0.06
0.00600	0.00200	5.94 ± 0.03

A free-radical chain reaction pathway for **1a** and triphenylphosphine was eliminated since the addition of the free-radical initiator azobisisobutyronitrile (0.001 M) did not change the rate of reaction (k_2 = 5.81 l. mole^{-1} min^{-1}) in nitromethane at 34.9 ± 0.01°. Addition of the inhibitor hydroquinone similarly gave k_2 = 5.99 ± 0.01 l. mole^{-1} min^{-1}.

The rate constants for aryl-substituted α-bromoacetophenones with triphenylphosphine in nitromethane are given in Table II. A Hammett plot of this data was done with a computer program developed by Professor M. Charton.[9] The use of σ_p values[10] gives $\rho = +0.423$ with a correlation coefficient $R = 0.985$. An excellent fit involved the use of $\sigma_p{}^\circ$ values[10] which gives $\rho = +0.4435$ (R = 0.996).

TABLE II
RATE CONSTANTS FOR THE REACTION OF TRIPHENYLPHOSPHINE AND *meta, para*-SUBSTITUTED α-BROMOACETOPHENONES IN NITROMETHANE AT 34.90 ± 0.01°

Bromo ketone[a]	Substituent	k_2, l. mole^{-1} min^{-1}	Rel k
Bromacetophenone **1a**		5.88 ± 0.07[b]	1.00
1b	p-CH$_3$O	5.43 ± 0.04	0.93
1c	p-CH$_3$	5.28 ± 0.10	0.91
1d	p-Br	8.48 ± 0.20	1.45
1e	p-NO$_2$	13.93 ± 0.13	2.40
1f	m-CH$_3$O	7.02 ± 0.18	1.20

[a] Initial concentrations used were 0.0100 M phosphine and 0.0100 M bromo ketone. [b] Later 5.84 ± 0.06 was found to be a better value and was used in activation energy calculations.

A brief comparison of solvents showed that the reactions of several of the bromoacetophenones are faster in nitromethane (dielectric constant 35.9 at 30°) than in acetonitrile (37.5 at 20°).[11] The relative rates of reaction of **1a**:**1c**:**1e** with triphenylphosphine in acetonitrile at 34.90 ± 0.01° are 1.00:0.97:2.41 (k_2 = 3.81 l. mole^{-1} min^{-1}, 3.70 ± 0.06 l. mole^{-1} min^{-1}, 9.18 ± 0.18 l. mole^{-1} min^{-1}, respectively).

The variation with temperature of the rates of reaction of **1a**, **1c**, **1e**, and **2** with triphenylphosphine gave kinetic data and activation quantities presented in Tables III and IV.

TABLE III
RATE CONSTANTS FOR REACTION OF TRIPHENYLPHOSPHINE AND HALOACETOPHENONES AT SEVERAL TEMPERATURES IN NITROMETHANE

Halo ketone	Temperature[a]	k_2, l. mole^{-1} min^{-1}
1a	0.0	0.633 ± 0.002
	34.9	5.84 ± 0.06
	46.8	11.79 ± 0.02
1c	34.9	5.28 ± 0.10
	46.8	11.74 ± 0.11
1e	0.0	1.60 ± 0.02
	34.9	13.93 ± 0.13
	46.8	27.35 ± 0.49
2	34.9	3.60 ± 0.14 × 10^{-2}
	45.1	6.12 ± 0.10 × 10^{-2}

[a] Temperature control at 34.9, 46.8, 45.1 was ±0.01°.

TABLE IV
ACTIVATION QUANTITIES FOR REACTION OF TRIPHENYLPHOSPHINE WITH α-HALOACETOPHENONES[a]

Halo ketone	E_a, kcal/mole	$\Delta H^\ddagger$, kcal/mole	$\Delta S^\ddagger$, eu
1a	10.86 ± 0.51[b]	10.3[b]	−29.9[b]
1c	12.38 ± 0.26	11.8	−27.4
1e	11.16 ± 0.54[b]	10.6[b]	−27.2[b]
2	10.12 ± 0.53[c]	9.5[c]	−42.5[c]

[a] From data at 34.9 and 46.8° unless otherwise stated. [b] From data at 0.0, 34.9 and 46.8°. [c] From data at 34.9 and 45.1°.

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[8] A. A. Frost and R. G. Pearson "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1965: (a) Chapter 3; (b) p 43.

[9] Kindly performed by Professor M. Charton, Pratt Institute.

[10] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

[11] Why the reactions in nitromethane are faster is not clear. Various possibilities are under consideration.

The rate constants for the reaction of several aryl-substituted bromoacetophenones with pyridine are given in Table V.

TABLE V

RATE CONSTANTS FOR REACTION OF PYRIDINE AND *meta*, *para*-SUBSTITUTED α-BROMOACETOPHENONES IN NITROMETHANE AT 34.9 ± 0.01°

Bromo ketone[a]	Substituent	k_2, l. mole^{-1} min^{-1}	Rel k
Bromoacetophenone **1a**		0.527 ± 0.003	1.00
1b	p-CH_3O	0.419 ± 0.004	0.80
1d	p-Br	0.767 ± 0.024	1.45
1e	p-NO_2	0.863 ± 0.001	1.64

[a] Initial concentrations used were 0.0100 M pyridine and 0.0100 M bromo ketone.

The use of σ_p values in the computer calculated Hammett plot gives $\rho = +0.303$ ($R = 0.923$) while the use of $\sigma_p{}^\circ$ values gives $\rho = +0.312$ ($R = 0.892$). The "confidence level" of these results is only 90% in contrast to the high R values for the phosphine kinetics.

The reaction of **2** with triphenylphosphine was found to be 44 times faster than with pyridine at 34.90 ± 0.01° ($k_2 = 3.60 \pm 0.14 \times 10^{-2}$ l. mole^{-1} min^{-1}; $8.13 \pm 0.05 \times 10^{-3}$ l. mole^{-1} min^{-1}, respectively).

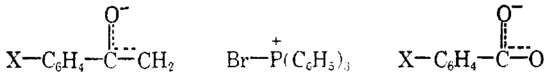
Discussion

The ρ value of +0.303 obtained by us for the reaction of bromoacetophenones with pyridine in nitromethane at 34.9° is in reasonable agreement with the small positive ρ values obtained for these reactions in acetone[12] (+0.55 at 20°) and in methanol[13] (+0.60 at 20°). The relative reaction rate of 65:1 for **1a**:**2** with pyridine in nitromethane also agrees reasonably well with the reported ratio of 54:1 in ethanol.[14] These reactions are probably best described by an SN2 type of mechanism with additional overlap of the entering group to carbonyl carbon in the transition state.[14]

The reaction ratio of 44:1 for triphenylphosphine: pyridine in reaction with **2** reflects the greater nucleophilicity of the phosphine in such displacement reactions. The triphenylphosphine:pyridine ratio for bromoacetophenone **1a** is 11:1. This smaller ratio for **1a**, compared with that for **2**, could be due to several factors. Since it appears that triphenylphosphine and pyridine both react with **1a** by bimolecular displacement of the bromide ion (see below) the smaller ratio for **1a** compared with **2** may be due simply to the greater reactivity (and lesser discrimination) of **1a** in nucleophilic displacements.

Of most importance in this present work is the finding of a small ρ value (+0.44) for the second-order bromoacetophenone–triphenylphosphine system in nitromethane. Such a small value is most easily explained by a mechanism involving bimolecular nucleophilic displacement of bromide ion by triphenylphosphine. Thus the reaction of **1a** with triphenylphosphine *under these conditions* appears to be quite similar to that of **2** with triphenylphosphine and to those of **1a** or **2** with pyridine.

The observed ρ value does not appear to be consistent with attack on bromine as usually pictured. Thus it is expected that initial displacement on bromine to give an enolate bromotriphenylphosphonium ion pair would be rate-determining (to be followed by a fast step involving ketophosphonium salt formation) and should give a ρ value comparable to that of the formation of benzoate from benzoic acid ($\rho = 1.000$ in water to 1.957 in ethanol is taken as the maximum range[12]). ρ values for the base-catalyzed formation of enolates from acetophenones are apparently not available.



$$\mathrm{X{-}C_6H_4{-}\overset{O^-}{C}{\cdots}CH_2}\qquad \mathrm{Br{-}\overset{+}{P}(C_6H_5)_3}\qquad \mathrm{X{-}C_6H_4{-}\overset{O^-}{C}{\cdots}O}$$

There is a possible complication that should be mentioned. Since the ρ value for the triphenylphosphine **1a** system is small, its sign might change with a moderate change of temperature depending upon the "isokinetic parameter temperature" β.[12] If one is measuring near the isokinetic temperature then a small positive ρ value might not necessarily be indicative of a negative charge buildup in the transition state. The only pertinent data on bromoacetophenone solvolysis is the known β value for the reaction of **1a** with aniline which is 210° K.[15] Such a temperature is safely removed from our operating temperatures.

Because of the above possibility and because activation parameters were desired, the rates of reaction of several of the bromoacetophenones with triphenylphosphine were found at several temperatures. The relative rates of **1a**:**1c**:**1e** at 46.8° (1:0.995:2.32) when compared to data at 34.9° (Table II) indicates that a similar ρ value will be found at the higher temperature. An approximate ρ value calculated from these points is +0.38. The **1a**:**1e** ratio at 0° is similarly 2.52.

The calculated activation enthalpy and entropy values for **1a**, **1c** (p-CH_3), **1e** (p-NO_2), and **2** in reaction with triphenylphosphine in nitromethane are all within the range for bimolecular nucleophilic displacement reactions in a polar solvent.[16]

The reaction of **2** with pyridine in nitromethane is about 12 times faster than the reported rate in methanol[17] even though the dielectric constants of the solvents are similar.[18] A similarly large rate difference in favor of nitromethane was noted in the reactions of tributylphosphine with ethyl iodide.[16a]

In view of the apparently accelerated rates of reaction in nitromethane and because of other reasons it was desired to determine the relative rates of reaction of the bromoacetophenones with triphenylphosphine in other solvents. The relative rates of reaction of **1a**:**1c**:**1e** with triphenylphosphine in acetonitrile, as presented above, indicates a ρ value similar (approximately +0.37 from the three points given) to that in

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[12] H. H. Jaffé, *Chem. Rev.*, **53**, 206 (1953).

[13] A. J. Sisti and W. Memeger, Jr., *J. Org. Chem.*, **30**, 2102 (1965).

[14] A. J. Sisti and S. Lowell, *Can. J. Chem.*, **42**, 1896 (1964).

[15] (a) J. C. Cox, *J. Chem. Soc.*, **119**, 142 (1921). (b) Most β temperatures are in the 300–400° K range.

[16] (a) W. A. Henderson, Jr. and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960). (b) References 7, 8. (c) Further studies on the observed differences for **1a** and **2** are in progress.

[17] R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, **74**, 5130 (1952).

[18] The dielectric constants of methanol 32.6 (25°) and nitromethane 35.9 (30°) were taken from "Technique of Organic Chemistry," Vol. VII, 2nd ed., A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1955, pp 270–274.

nitromethane. Preliminary experiments[19] in benzene indicate that the **1e** (p-NO$_2$):**1a** reaction rate ratio with triphenylphosphine is between 2.1 and 3.0 (Experimental Section). This was determined from the competition of equimolar amounts of **1e** and **1a** for triphenylphosphine in benzene wherein 32–37% of **1e** and 63–68% of **1a** were found to be unreacted by nmr. This suggests that the ρ value in benzene is not too different from that in nitromethane and that it is still significantly below 1.

It thus appears that **1a** is converted to the ketophosphonium bromide **3a**, at least under the conditions studied in nitromethane and acetonitrile, *via* S$_N$2 type of displacement of bromide ion. The present results are not necessarily valid for other bromo ketones. The relationship of the present data to the debromination of **1a** with triphenylphosphine and protic species is now being explored. It is recognized that a more sensitive mechanistic test would involve the use of a benzylic bromo ketone series. We hope to investigate such a series.

Experimental Section

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Beckman IR-8. Nmr spectra were recorded on a Varian A-60A spectrometer with tetramethylsilane as an internal standard. Thin layer chromatography was done on Brinkman silica gel HF$_{254}$ using mainly 5% ethyl acetate–benzene as the developing solvent.

The following compounds were obtained commercially and recrystallized to a constant melting point and tlc purity (one spot): triphenylphosphine, bromoacetophenone, chloracetophenone, p-nitro-α-bromacetophenone, and p-bromo-α-bromoacetophenone.

Pyridine was stirred overnight with potassium hydroxide pellets and then distilled from calcium oxide through a glass helices packed column. The fraction of bp 115.5° was used.

Spectrograde (Eastman Kodak) nitromethane was dried and distilled from calcium chloride through a glass helices packed column. The fraction of bp 100.7° (lit.[20] bp 100.8°) was used for kinetic studies. Acetonitrile (Fisher reagent) was dried and distilled from phosphorus pentoxide. The fraction of bp 81.0° (lit.[20] bp 80.06°) was used for kinetic studies. Other solvents were dried and distilled by common procedures.

p-Methoxy-α-bromoacetophenone (Ib).—To a solution of p-methoxyacetophenone (10 g, 0.067 mole) in carbon tetrachloride (100 ml) was added bromine (10.66 g, 0.067 mole) dropwise with stirring. After being stirred for 3 hr the reaction mixture was washed with sodium bisulfite and dried, and the solvent was removed *in vacuo*. The crude product was recrystallized four times from 30–60° petroleum ether to give Ib, 7 g (46%) of white crystals, mp 69–70°, only one spot (tlc) above that for starting material. The nmr (CCl$_4$) of Ib exhibited a 4 H A$_2$B$_2$ quartet centered at τ 2.5 (aromatic protons), a 2 H singlet at τ 5.5 (methylene), and a 3 H singlet at 6.0 (methoxy).

m-Methoxy-α-bromoacetophenone (If).—The bromination of m-methoxyacetophenone, as for Ib, gave If as white flakes after five recrystallizations from 95% ethanol, mp 61–62°. The nmr (CDCl$_3$) exhibited 4 H aromatic proton absorption at τ 2.5, 2.6–3.0, a 2 H singlet at 5.5 (methylene), and a 3 H singlet at 6.0 (methoxy).

p-Methyl-α-bromoacetophenone (Ic).—To a stirred suspension of aluminum chloride (49 g, 0.372 mole) in carbon disulfide (100 ml) was added a solution of bromoacetyl bromide (50 g, 0.248 mole) in dry toluene (22.8 g, 0.248 mole) over a 1.5-hr period. The reaction mixture was then warmed on a steam bath for 1 hr and poured slowly over ice; the organic layer was extracted into ether. The ether layer was washed several times each with sodium carbonate and then water, dried over magnesium sulfate, and evaporated to leave a brown solid which was recrystallized four times from 30–60° petroleum ether to give Ic, 35 g (66%) as white needles, mp 51–52° (lit.[21] mp 48–50°), one spot (tlc). The nmr (CCl$_4$) of Ic exhibited a 4 H A$_2$B$_2$ quartet centered at τ 2.4, a 2 H singlet at 5.6 and a 3 H singlet at 7.6.

Anal. Calcd for C$_9$H$_9$Br: C, 50.73; H, 4.26; Br, 37.50. Found: C, 51.03; H, 4.29; Br, 37.87.

Reaction of α-Bromoacetophenones with Pyridine and Triphenylphosphine.—Several of the bromo ketones were treated with pyridine or triphenylphosphine to give genuine samples of pyridinium or triphenylphosphonium[22] bromides. Nitromethane and other solvents were used for these reactions.

Competition Experiments.—A mixture of **1a** (2.010 g) and **1e** (2.436 g, 0.010 mole each) in dry benzene (20 ml) was treated with triphenylphosphine (2.715 g, 0.010 mole) in benzene (15 ml) at reflux. After two hr (no phosphine left by tlc) a mixture of phosphonium salts (5.001 g) was obtained. Nitrogen analyses of 1.79 and 1.68% were obtained for the mixture. This corresponds to 63% of the p-nitro salt from **1e** and 37% of the salt from **1a**. Use of the equation[23]

$$\frac{k_2(p\text{-NO}_2)}{k_2(\text{H})} = \frac{\log \dfrac{[\mathbf{1e}]_i}{[\mathbf{1e}]_f}}{\log \dfrac{[\mathbf{1a}]_i}{[\mathbf{1a}]_f}}$$

gives a relative rate ratio of 2.96. The calculated % N for the pure phosphonium salt from **1e** is 2.77.

In a similar experiment the phosphonium salts were removed and the ratio of unreacted **1a**:**1e** was determined to be 68:32 by comparison of their methylene peaks in benzene by nmr. The peaks were assigned by comparison with pure **1a** and **1e** and the ratio is an average of three integrations. This gives a relative rate ratio for **1e**:**1a** of 2.14.

Calibration Curves.—In a typical procedure, a calibration curve relating the conductivity of **3** to its concentration in solution was prepared as follows. The resistance of a solution of **3** (0.131 g) in nitromethane (50 ml) was measured at 34.9° in one of the conductivity cells used in the kinetic studies. The resistance was measured for the solution at one-half and one-quarter concentration, the resistance values were converted to conductance values and the conductance was graphically plotted against concentration to give a straight line. The "infinite resistance" values (see below) obtained in actual kinetic runs were converted to conductance values and were related to concentration of phosphonium salts from the calibration curves. In this manner the reaction of triphenylphosphine with **1a** was shown to proceed to 96–98% in the kinetic runs.

Kinetic Method.—Solutions of triphenylphosphine or pyridine and the appropriate halo ketone, usually 0.02 M each in nitromethane or acetonitrile, were equilibrated in volumetric flasks placed in a constant-temperature bath. A constant-volume sample of the halo ketone was withdrawn (all operations were done under nitrogen) with a standardized gas-tight Hamilton syringe fitted with a Chaney adapter and introduced through a rubber septum into a conductivity cell which had been previously flushed with nitrogen. The conductivity cells were fitted with two rubber-capped Teflon stopcocks and a septum-containing central joint to allow transfer of solutions under nitrogen. After the cell was brought to constant temperature an equal volume of a triphenylphosphine or pyridine solution was injected, the cell was agitated in the bath for 30 sec and resistance readings were taken for at least three half-lives. The appearance of phosphonium or pyridinium salts were followed by the decrease in resistance at 1000 cps using a Thomas-Serfass bridge. The "infinite resistance," R_∞, was obtained as the constant resistance of the solution after 15–20 half-lives. At the end of a run the solution was examined by tlc to show only the phosphonium or pyridinium salts in essentially every case. Significantly no debrominated ketones were found (by tlc) in the triphenylphosphine reactions. Thus any

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[19] K. Kirby, research in progress.

[20] "Handbook of Chemistry and Physics," 45th ed, R. C. Weast, Ed., The Chemical Rubber Co., Cleveland, Ohio, 1964.

[21] "Dictionary of Organic Compounds," Vol. I, I. Heilbron, Ed., Oxford University Press, 1965, p 459.

[22] A. V. Dombrovskii and M. I. Shevchuk, *J. Gen. Chem., USSR*, **33**, 1263 (1963).

[23] G. Russell in "Technique of Organic Chemistry," Vol. VIII, part I, 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961.

moisture present in the polar solvents used did not alter the phosphonium salt formation.[24]

Calculation of Rate Constants and ρ Values.—Over-all second-order rate constants for the equal initial concentration runs were calculated by graphically plotting $R/R - R_\infty$ *vs.* time, where R is the resistance at the time t and R_∞ is the infinite resistance. The rate constants were then obtained from the slope of the linear second-order plot.[8] Two or more kinetic runs were usually performed for each set of compounds under a given set of conditions, the observed rate constants were averaged and the uncertainty was expressed as the standard deviation of their mean. Reproducibility of 1–2% was usually found.

For the unequal initial concentration runs each resistance reading was converted to a conductance value and divided by the conductance for 100% reaction to give the per cent of phosphonium salt for each time. From this the actual concentration of salt at time t was determined and the quantity $\log b(a - x)/[a(b - x)]$ was calculated for each time t. This quantity was plotted against time to give a straight line from whose slope the second-order rate constants were determined from the usual second-order equation.

Approximate (three point) Hammett ρ correlations were done by the usual plotting of $\log k/k_0$ *vs.* σ values. The more precise ρ values obtained from the data given in Tables II and V were calculated by M. Charton.[9]

Registry No.—**1a**, 70-11-1; **1b**, 2632-13-5; **1c**, 619-41-0; **1d**, 99-73-0; **1e**, 99-81-0; **1f**, 5000-65-7; **2**, 532-27-4; triphenylphosphine, 603-35-0.

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[24] We have found that 1 equiv of methanol causes much less dehalogenation in the **1a**–triphenylphosphine system in acetonitrile than in benzene.[19] Furthermore k_2 is only slightly less for this system (Table II) in the presence of 1 equiv of ethanol.

The Reaction of α-Halo Oximes with Triphenylphosphine. Formation of Imidoyl Bromide and of Oximinophosphonium Salts by a Novel Catalytic Effect of Bases

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The reaction of 2-bromoacetophenone oximes with triphenylphosphine was investigated. Under ordinary condition a Beckmann rearrangement occurred and the product was N-phenylacetimidoyl bromide. In view of this result, the reaction of keto oximes with triphenylphosphine dibromide was examined and a new synthesis of ketenimines was developed. In the presence of a trace of bases, the reaction of 2-bromoacetophenone oximes with triphenylphosphine led to exclusive formation of oximinophosphonium salts. The oximinophosphonium salts were treated with base to yield the dehydrobrominated products, whose structure and reactions were studied.

The reactions of α-halocarbonyl compounds with tertiary phosphines have been reported by many workers to afford either 2-oxophosphonium salts or various products *via* enolphosphonium salts.[1] In an extention of this reaction to α-halo oximes, it might be expected that 2-oximinophosphonium salts or other products *via* intermediates analogous to enolphosphonium salts would be formed. In the present paper, we report the reactions of 2-bromoacetophenone oximes (**1**) with triphenylphosphine (**2**), which resulted in the formation of acetimidoyl bromides (**3**) and of 2-oximinophosphonium salts (**12**) by a novel catalytic effect of bases.

2-Bromoacetophenone oxime was recorded by Korten and Scholl to be obtainable as prisms or needles with mp 92° in the treatment of 2-bromoacetophenone with 3 equiv of hydroxylamine hydrochloride in aqueous methanol;[2] the product has been believed to be almost pure in the recent papers.[3] However, the nmr analysis of the product revealed that the procedure gave only a mixture of 2-bromoacetophenone oxime (τ 5.63, 2 H) and a considerable amount of 2-chloroacetophenone oxime (τ 5.45, 2 H) which was formed by replacement of bromine with chlorine during the oximination. 2-Bromoacetophenone oxime (**1a**) could be obtained in a pure form with mp 97–98° by treatment of 2-bromoacetophenone with hydroxylamine hydrobromide in methanol. Some 4′-substituted 2-bromoacetophenone oximes were prepared by this procedure and the constants are summarized in Table I.

When **1a** was treated with triphenylphosphine (**2**) in absolute acetonitrile at room temperature, a trace of hydrogen bromide was evolved and N-phenylacetimidoyl bromide (**3a**) was formed together with triphenylphosphine oxide (**4**). The formation of **3a** was confirmed by treatment of the reaction mixture with water or aniline at room temperature, giving acetanilide or N,N′-diphenylacetamidine in *ca.* 40% yield. In the treatment with aniline, a trace of N,N′-diphenylanilinoacetamidine was also isolated.

Analogous reactions of 2-bromo-4′-nitroacetophenone oxime (**1b**), 2-bromo-4′-methylacetophenone oxime (**1c**), and 2-bromo-4′-chloroacetophenone oxime (**1d**) with **2** resulted in the formation of the corresponding acetimidoyl bromides (**3b**, **3c**, and **3d**) and **4**.

A probable pathway for this reaction would involve an initial nucleophilic attack of tricovalent phosphorus

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[1] See, for example, (a) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957); (b) S. Trippett, *J. Chem. Soc.*, 2337 (1962); (c) I. J. Borowitz and L. I. Grossman, *Tetrahedron Letters*, 471 (1962); (d) H. Hoffman and H. J. Diehr, *ibid.*, 583 (1962); (e) A. J. Speziale and L. R. Smith, *J. Am. Chem. Soc.*, **84**, 1868 (1962); (f) R. D. Partos and A. J. Speziale, *ibid.*, **87**, 5068 (1965); (g) P. A. Chopard, R. F. Hudson, and G. Klopman, *J. Chem. Soc.*, 1379 (1965); (h) I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

[2] H. Korten and R. Scholl, *Ber.*, **34**, 1907 (1901).

[3] (a) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962); (b) M. Masaki, M. Sugiyama, S. Tayama, and M. Ohta, *Bull. Chem. Soc. Japan*, **39**, 2745 (1966).