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.

Acknowledgment.—We are indebted to Dr. Grace Borowitz, Dr. Martin Grayson, and Professor Cheves Walling for stimulating discussions and to Professor M. Charton for the computor-calculated Hammett ρ values.

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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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Received July 10, 1967

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).

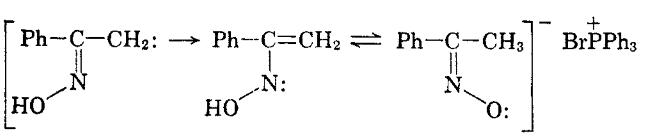
TABLE I

4′-SUBSTITUTED 2-BROMOACETOPHENONE OXIMES

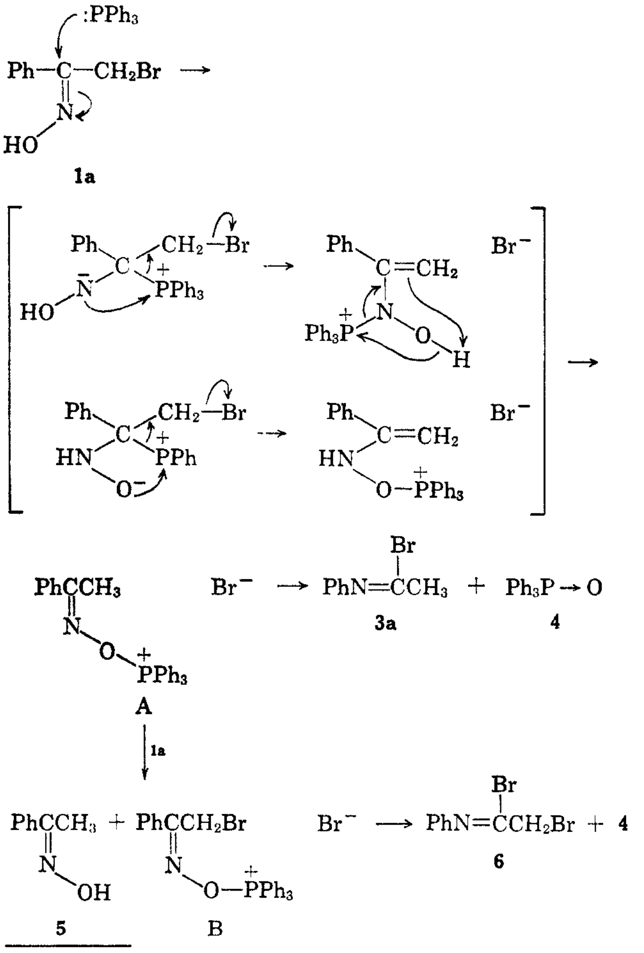
Substituent	Yield, %	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
H	75	98–99[a]	C_8H_8NOBr	44.86	3.74	6.54	45.08	4.08	6.76
NO_2	90	129–129.5[b]	$C_8H_7N_2O_3Br$	37.07	2.74	10.81	37.35	2.74	11.00
CH_3	86	117–118.5[c]	$C_9H_{10}NOBr$	47.37	4.39	6.14	47.70	4.61	6.10
Cl	94	118.5–119[c]	$C_8H_7NOBrCl$	38.63	2.82	5.63	38.58	2.56	5.72
CH_3O	83	101–102.5[c]	$C_9H_{10}NO_2Br$[d]	44.26	4.10	5.74	44.56	4.15	5.65

[a] See Experimental Section. [b] Recrystallized from benzene. [c] Recrystallized from ligroin. [d] Registry no. 14181-83-0.

on the oxime carbon[4] followed by migration of electrons and atomic groups to give a quasiphosphonium salt (A),[5] which then underwent a Beckmann rearrangement to yield **3a** and **4**, as illustrated in Scheme I. The formation of a trace of N,N′-diphenylanilinoacetamidine isolated from the treatment with aniline may be reasonably explained as follows. A reaction of A with **1a** occurred to small extent to yield acetophenone oxime (**5**) and a quasiphosphonium salt (B), which underwent a Beckmann rearrangement to give N-phenylbromoacetimidoyl bromide (**6**); the latter would transform to the anilinoacetamidine on the treatment with aniline. The evolution of hydrogen bromide may be ascribed to bimolecular condensation of **3a**.[6]



SCHEME I

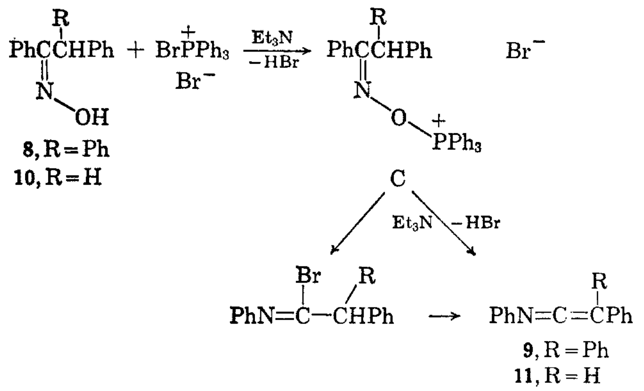


Analogous quasiphosphonium salts have been postulated in the reaction of benzaldoxime with triphenylphosphine dibromide (**7**)[7] and in the reaction of *gem*-chloronitroso- or *gem*-chloronitrocycloalkane with **2**.[8] Thus, the reaction of **5** with **7** would result in the formation of **3a**. When both reactants were treated in the presence of 1 equiv of triethylamine under conditions similar to those used for the reaction of **1a** with **2**, the imidoyl bromide was formed in a 40% yield.[9]

These reactions for the formation of imidoyl bromide appeared to be advantageous in *in situ* preparative methods. Stevens and French reported that some ketenimines could be obtained from imidoyl chlorides by treating with triethylamine in acetone or boiling benzene.[10] Thus, in the above reaction with **7**, the use of 1 equiv more of triethylamine would lead to the formation of ketenimine.

When diphenylacetophenone oxime (**8**) was treated with **7** in the presence of 2 equiv of triethylamine in acetonitrile at room temperature, diphenylketene-N-phenylimine (**9**) was, as expected, obtained in 45% yield. Although the formation of ketenimine is explained either by loss of hydrogen bromide from imidoyl bromide or by a rearrangement of the quasiphosphonium salt (C) accompanied with direct deprotonation (Scheme II), this reaction is the first ex-

SCHEME II



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(4) Some possibilities of a reaction path involving an initial attack of phosphorus on carbonyl carbon have been shown: (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, p 159; (b) D. B. Denney, N. Gershman, and J. Giacin, *J. Org. Chem.*, **31**, 2833 (1966).

(5) In view of a mechanism proposed for the reaction of α-halocarbonyl compound with tertiary phosphine,[4a–b] a reaction course *via* an ion pair intermediate appears also attractive. Initial displacement by phosphorus on bromine of **1a** to give an enaminate bromophosphonium ion pair and the subsequent recombination of the latter would lead to the formation of the quasiphosphonium salt (A).

(6) The corresponding chloride has been reported to be susceptible to thermal bimolecular condensation through loss of hydrogen chloride: J. von Braun, *Angew. Chem.*, **47**, 614 (1934); T. L. Cairns, P. J. Graham, P. L. Barrick, and R. S. Schreiber, *J. Org. Chem.*, **17**, 751 (1952).

(7) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959).

(8) M. Ohno and I. Sakai, *Tetrahedron Letters*, 4541 (1965); M. Ohno and N. Kawabe, *ibid.*, 3935 (1966).

(9) The yield was based on conversion to the corresponding acetanilide or acetamidine.

(10) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954).

ample of direct formation of a ketenimine from a ketoxime. An analogous treatment of desoxybenzoin oxime (**10**) below 0° afforded phenylketene-N-phenylimine (**11**) in 75% yield, a preparation of which appeared to be impracticable by other methods[10,11] since **11** was a thermally unstable substance.

In the reaction of **1a** with **2** in either acetonitrile, benzene, chloroform, or tetrahydrofuran, no 2-oximinophosphonium salt (**12a**) was formed. However, it was found that, if a trace of base was present, the same reaction led to exclusive formation of **12a**. Treatment of **1a** with **2** in the presence of a few drops of an aqueous solution of potassium cyanide in acetonitrile afforded readily 87% yield of (2-phenyl-2-oximinoethyl)triphenylphosphonium bromide (**12a**).

A similar catalytic effect was observed by using other bases, such as an aqueous solution of sodium cyanide, potassium hydroxide, sodium hydroxide or potassium carbonate, triethylamine, or pyridine. These catalysts were also effective for the formation of 2-oximinophosphonium salts in the reactions of 2-bromo-4′-nitroacetophenone oxime (**1b**), 2-chloroacetophenone oxime (**13**), and 3-chloro-2-oximinopropiophenone (**14**) with **2**; the results are summarized in Table II.

TABLE II

REACTION OF α-HALO OXIMES WITH TRIPHENYLPHOSPHINE

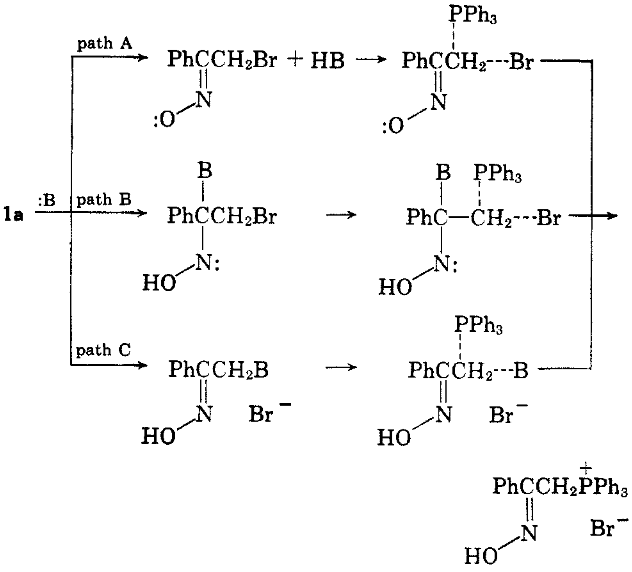
α-Halo oxime	Without catalyst		With catalyst	
	Reaction time, hr	Yield of 2-oximinophosphonium salt, %	Reaction time, hr	Yield of 2-oximinophosphonium salt, %
1a	6	0	2	87[a]
			2	88[b]
			2	76[c]
			1	68[d]
1b	6	0	2	93[a]
			2	88[b]
13	23	44	2	93[a]
	72	73		
14	6	53	2	96[a]
	35	88		

[a] Catalyst: 33% aqueous potassium cyanide. [b] Triethylamine. [c] 8% aqueous sodium hydroxide. [d] Pyridine.

In view of the consideration of the formation of imidoyl bromide from **1** and **2**, the base-catalyzed reaction for the formation of 2-oximinophosphonium salt might be explained by three paths: an attack by phosphorus on α carbon in the conjugate base of the oxime (path A), an initial attack of base on the oxime carbon followed by displacement of bromine with **2** (path B), or the preliminary replacement of bromine with base followed by displacement with **2** (path C), as shown in Scheme III.

Path C was ruled out by control experiments, which showed that (2-phenyl-2-oximinoethyl)pyridinium bromide neither reacted with **2** nor catalyzed the reaction of **1a** with **2**, whereas a catalytic amount of pyridine led to the exclusive formation of **12a** under the identical condition. Although there is no positive evidence, the catalytic reaction may be rationalized by path A or B,[12] which would have somewhat of an S_N1 character since the transition states are stabilized by mesomeric electron release from the nearby anionic sites.[13]

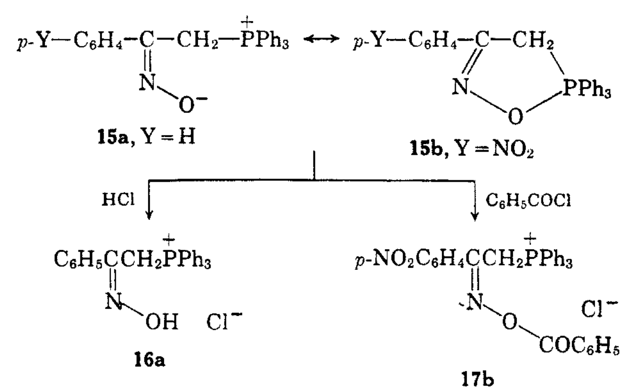
SCHEME III



12a

The phosphonium bromide (**12a**) was treated with potassium hydroxide, triethylamine, or ammonium hydroxide to give a dehydrobrominated product (**15a**) in a quantitative yield. Analogous treatment of [2-(4-nitrophenyl)-2-oximinoethyl]triphenylphosphonium bromide (**12b**) afforded the dehydrobrominated product (**15b**). The nmr data and the elemental analytical data as well as the reactions suggested a betaine structure or its related cyclic structure for **15**. The nmr spectrum of **15a** showed two multiplets at τ 2.7 and 2.4 and a doublet at 6.6. The ratio of the peak areas (two multiplets, a doublet) was 22:2 (the theoretical value is 20:2). Treatment of **15a** with hydrogen chloride gave (2-phenyl-2-oximinoethyl)triphenylphosphonium chloride (**16a**), which was identical with the product obtained by the reaction of **13** with **2** (Scheme IV). Reaction of **15b** with benzoyl chloride afforded [2-(4-nitrophenyl)-2-benzoyloximinoethyl]triphenylphosphonium chloride (**17b**), which exhibited strong infrared absorption at 1745 and 1250 cm^{-1}, typical of ester groups.

SCHEME IV



15a, Y = H

15b, Y = NO$_2$

16a

17b

The product **15a** is stable in crystalline form, but,

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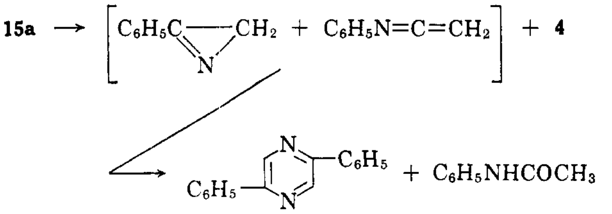
[11] C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **75**, 657 (1953); C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964).

[12] A mechanism involving initial attack of phosphorus on bromine appeared impractical since the action of base on the oxime would markedly decrease the electron-withdrawing character of α carbon.

[13] Analogous "borderline S_N2" transition states have been postulated often in epoxide chemistry: A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," Part One, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 270.

upon being heated in benzene, chloroform, tetrahydrofuran, or alcohol, readily decomposed to afford triphenylphosphine oxide; a trace of 2,5-diphenylpyrazine was isolated and the formation of acetanilide was confirmed (Scheme V).

SCHEME V



These facts suggested that **15a** would give azirine and ketenimine under loss of **4** upon pyrolysis[14] (Scheme V). This behavior is closely related to that of vinyl azide.[15]

Experimental Section

Acetonitrile used was distilled from phosphorus pentaoxide and redistilled from potassium carbonate. Benzene was distilled from sodium. All concentrations and evaporations were carried out under reduced pressure. All melting points were determined in a liquid bath and are uncorrected.

2-Bromoacetophenone Oxime (1a).—A solution of 2-bromoacetophenone (10 g, 0.05 mole) and hydroxylamine hydrobromide (17.2 g, 0.15 mole) in methanol (150 ml) was allowed to stand at room temperature overnight. The mixture was poured into a large amount of water and the crystalline oxime was collected and dried (8.1 g). Recrystallization from ligroin gave colorless needles. The nmr spectrum (60 Mc, $CDCl_3$) exhibited a multiplet at τ 2.57 (5 H) and a singlet at 5.63 (2 H).

Reaction of 1a with Triphenylphosphine (2) in the Absence of Catalyst.—A solution of **1a** (2.14 g, 0.01 mole) in acetonitrile (30 ml) was added dropwise, with stirring, to a solution of **2** (2.62 g, 0.01 mole) in acetonitrile (60 ml). The stirring was continued at room temperature. The solution assumed a pale yellow color gradually with a slight evolution of hydrogen bromide, which was detected by pH test paper and by conversion into silver bromide (*ca.* 10% yield). After 6 hr, the reaction mixture was treated with water or aniline.

A. Treatment with Water.—To the mixture was added water (1 ml). After 18 hr, the solution was concentrated and the brown oily residue was dissolved in ethanol (10 ml). To the solution was added a hot solution of zinc chloride ($ZnCl_2$; 1.36 g, 0.01 mole) in ethanol (5 ml) and the mixture was allowed to stand for several hours. After removal of the zinc chloride complex of triphenylphosphine oxide (2.82 g, 68%; mp 231°, lit.[16] mp 229–230°), the solution was concentrated and chromatographed on an unactivated alumina column. Elution with benzene afforded acetanilide (0.58 g, 44%), which was identical, in melting point and infrared spectrum, with an authentic sample.

B. Treatment with Aniline.—To the mixture was added a solution of aniline (0.93 g, 0.01 mole) in acetonitrile (10 ml). After 50 hr, the mixture was concentrated to give a brown oily residue, to which 1 *N* hydrochloric acid and benzene were added. The aqueous layer was neutralized with sodium bicarbonate to separate crystalline and oily substances. The crystalline substance, N,N′-diphenylacetamidine, was collected and dried (0.85 g, 41%). Recrystallization from ligroin give colorless needles, mp 131.5° (lit. mp 131–132°,[17a] 132°[17b]). The oily substance was treated with a small quantity of ethanol to give N,N′-diphenylanilinoacetamidine as needles (0.05 g, 1.7%). Recrystallization from ethanol afforded colorless needles, mp 178.5–181.5° (lit.[18] mp 189–190°).

Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.59; H, 6.33; N, 14.09.

The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was treated with zinc chloride in ethanol to give the complex of triphenylphosphine oxide (2.86 g, 69%). Reaction of **1a** with **2** in benzene led to the same results.

Reaction of 4′-Substituted 2-Bromoacetophenone Oximes with 2 in the Absence of Catalyst.—In a manner analogous to that described for the reaction of **1a** with **2**, a solution of 0.01 mole of 2-bromo-4′-nitroacetophenone oxime (**1b**), 2-bromo-4′-methylacetophenone oxime (**1c**), or 2-bromo-4′-chloroacetophenone oxime (**1d**) in acetonitrile (30 ml) was treated with **2** (0.01 mole) dissolved in acetonitrile (60 ml). The formation of N-(4-nitrophenyl)acetimidoyl bromide in 36% yield, N-(4-methylphenyl)acetimidoyl bromide in 83% yield, or N-(4-chlorophenyl)acetimidoyl bromide in 66% yield was confirmed by treatments of the reaction mixture with water or aniline, giving the corresponding acetanilide or acetamidine.

Reaction of Acetophenone Oxime (5) with Triphenylphosphine Dibromide (7).—To a suspension of **7**, prepared from **2** (2.62 g, 0.01 mole) in benzene (30 ml) and bromine (1.6 g, 0.01 mole) in benzene (5 ml), was added a solution of triethylamine (1.01 g, 0.01 mole) in benzene (10 ml) at 0–6° with ice cooling. To the mixture was added dropwise a solution of **5** (1.35 g, 0.01 mole) in benzene (25 ml) with stirring at the same temperature. The resultant mixture was stirred at room temperature for 6 hr and then treated with water or aniline in the same manner as for the reaction of **1a** with **2**. In the treatment with water there were obtained acetanilide (41% yield) and triphenyl phosphine oxide (77% yield). Treatment with aniline gave N,N′-diphenylacetamidine (41% yield) and triphenylphosphine oxide (97% yield).

Diphenylketene-N-phenylimine (9).—To a solution of **7**, prepared from **2** (4.85 g, 0.0185 mole) in acetonitrile (80 ml) and bromine (2.96 g, 0.0185 mole) in acetonitrile (10 ml), was added a solution of triethylamine (3.74 g, 0.037 mole) in acetonitrile (10 ml) dropwise under cooling and then a solution of diphenylacetophenone oxime[19] (5.32 g, 0.0185 mole) in acetonitrile (100 ml) was added dropwise with stirring. The mixture was stirred at room temperature for 2 hr and concentrated by rotary evaporation. The residue was extracted with *n*-hexane (50 ml). Evaporation of the solvent afforded the ketenimine **9** (2.0 g), the infrared spectrum of which was superimposable on that of the authentic sample.[20] The residue from the *n*-hexane extraction was treated with benzene and the solution, after removal of the insoluble triethylamine hydrobromide, was concentrated to give a reddish brown residue, which was extracted with petroleum ether (bp 30–60°). Evaporation of the extract afforded more **9**, which was hydrolyzed with 3 *N* hydrochloric acid to give diphenylacetanilide (0.23 g, 4.3%), mp 179.5°, which showed no depression on admixture with an authentic sample,[20] mp 182°. The total yield of **9** was 45%. The residue from petroleum ether extraction was treated with zinc chloride in ethanol to give the complex of triphenylphosphine oxide (4.35 g, 58%).

Phenylketene-N-phenylimine (11).—To a suspension of **7**, prepared from **2** (6.5 g, 0.025 mole) in acetonitrile (60 ml) and bromine (4 g, 0.025 mole) in acetonitrile (20 ml), was added a solution of triethylamine (5 g, 0.05 mole) in acetonitrile (10 ml) and then a solution of desoxybenzoin oxime (6 g, 0.025 mole) in acetonitrile (30 ml) was added dropwise with stirring at temperatures between −5 and −10° (ice-salt cooling). The mixture was stirred below 0° for 2 hr and concentrated by rotary evaporation. The residue was extracted twice with petroleum ether (bp 45–80°) and the extract was concentrated by rotary evaporation to about half volume. The separated crystalline or oily materials were removed by filtration and the filtrate was further concentrated to give the ketenimine **11** as a

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[14] A detailed investigation on the pyrolysis of **15** was then projected. During the investigation, however, the synthesis and pyrolysis of analogous compounds were communicated by German workers. H. J. Bestmann and R. Kunstmann [*Angew. Chem.*, **78**, 1060 (1966)] reported that the reaction of benzonitrile oxide with isopropylidenetriphenylphosphorane gave a betaine, dimethyl homolog of **15a**, the pyrolysis of which yielded the corresponding azirine. Analogously, R. Huisgen and J. Wulff [*Tetrahedron Letters*, 917 (1967)] obtained **15a** by the reaction of benzonitrile oxide and methylenetriphenylphosphorane and proposed a cyclic structure for **15a** on the basis of P^{31} nmr data.

[15] G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); G. R. Harvey and K. W. Ratts, *ibid.*, **31**, 3907 (1966).

[16] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

[17] (a) R. Biedermann, *Ber.*, **7**, 540 (1874); (b) M. Busch and R. Hobein, *ibid.*, **40**, 4296 (1907).

[18] R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 80 (1928).

[19] W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 5587 (1956).

[20] The sample was supplied by K. Ichimura; *cf. Tetrahedron Letters*, 807 (1966).

yellow oil (4.1 g, 74%), which was a thermally labile substance and characterized by a strong infrared absorption at 2020 cm^{-1} and by conversion into phenylacetanilide, mp 114.5–116° (lit. mp 116°,[21a] 116–117°[21b]).

(2-Phenyl-2-oximinoethyl)triphenylphosphonium Bromide (12a).—To a solution of **2** (2.62 g, 0.01 mole) in acetonitrile (50 ml) were added, with stirring, 5 drops of 33% aqueous potassium cyanide and then a solution of **1a** (2.14 g, 0.01 mole) in acetonitrile (30 ml). After 2 hr, the crystalline precipitate was collected and dried (4.15 g). The analytical sample was obtained by recrystallization from water, colorless prisms, mp 232–233° dec. The infrared spectrum (KBr) showed absorption bands at 3050–2900 (br), 2810, 2720, 1435, 1110, and 952 cm^{-1}.

Anal. Calcd for $C_{26}H_{23}NOPBr$: C, 65.55; H, 4.83; N, 2.94. Found: C, 65.71; H, 5.05; N, 3.15.

In place of aqueous potassium cyanide as catalyst, there were effectively used aqueous sodium cyanide (2 drops of a 33% solution), aqueous sodium hydroxide (2 drops of an 8% solution), aqueous potassium carbonate (10 drops of a 33% solution), triethylamine (2 drops), and pyridine (2 drops) in each 0.01 mole scale reaction. The results are shown in Table II.

[2-(4-Nitrophenyl)-2-oximinoethyl]triphenylphosphonium Bromide (12b).—The same directions were followed as for **12a**. From **1b** (2.59 g, 0.01 mole) and **2** (2.62 g, 0.01 mole) in the presence of 33% aqueous potassium cyanide (5 drops) or triethylamine (2 drops) there was obtained the phosphonium bromide (**12b**, 4.82 g). Recrystallization from ethanol afforded yellowish prisms, mp 225.5° dec. The infrared spectrum (KBr) showed absorption bands at 3060–2970 (br), 2900, 2820, 2710, 1520, 1440, 1110, 965, and 855 cm^{-1}.

Anal. Calcd for $C_{26}H_{22}N_2O_3PBr$: C, 59.88; H, 4.22; N, 5.37. Found: C, 59.42; H, 4.29; N, 5.84.

(2-Phenyl-2-oximinoethyl)triphenylphosphonium Chloride (16a). A. In the Absence of Catalyst.—A solution of 2-chloroacetophenone oxime (**13**) (0.85 g, 0.005 mole) in acetonitrile (5 ml) was added to a solution of **2** (1.31 g, 0.005 mole) in acetonitrile (15 ml) and the resultant solution was stirred at room temperature for 23 hr. The precipitated phosphonium chloride was collected by filtration (0.95 g). The analytical sample was obtained by recrystallization from ethanol–ethyl acetate yielding colorless prisms, mp 219–220° dec. The infrared spectrum (KBr) was essentially identical with the corresponding bromide **12a**.

Anal. Calcd for $C_{26}H_{23}NOPCl$: C, 72.31; H, 5.33; N, 3.24. Found: C, 72.07; H, 5.43; N, 3.48.

The above acetonitrile filtrate was allowed to stand at room temperature. The phosphonium chloride precipitated additionally and the result is shown in Table II.

B. In the Presence of Catalyst.—Reaction on the same scale was carried out in the presence of 3 drops of 33% aqueous potassium cyanide. After 2 hr, the crystalline precipitate was collected (2.0 g) and confirmed to be identical with the substance obtained from the noncatalytic reaction.

(3-Phenyl-3-oxo-2-oximinopropyl)triphenylphosphonium Chloride.—In the same manner as for **16a**, 3-chloro-2-oximinopropiophenone (1.97 g, 0.01 mole) was treated with **2** (2.62 g, 0.01 mole) in acetonitrile (30 + 50 ml) in the absence or presence of 5 drops of 33% aqueous potassium cyanide. The yields were shown in Table II. Recrystallization from ethanol afforded colorless prisms, mp 221.5° dec. The infrared spectrum (KBr) showed absorption bands at 3050, 2900, 2800, 2700, 2625, 1650, 1440, 1110, 1030, and 945 cm^{-1}.

Anal. Calcd for $C_{27}H_{23}NO_2PCl$: C, 70.50; H, 5.29; N, 3.08. Found: C, 70.51; H, 5.01; N, 3.05.

(2-Phenyl-2-oximinoethyl)pyridinium Bromide.—A solution of pyridine (1.58 g, 0.02 mole) in acetonitrile (20 ml) was added dropwise, with stirring and ice cooling, to a solution of **1a** (4.28 g, 0.02 mole) in acetonitrile (40 ml). The precipitated pyridinium bromide was collected (5.2 g, 89%) and recrystallized from ethanol to give colorless needles, mp 204° dec. The infrared spectrum (KBr) showed absorption bands at 3150–2950 (br), 1640, 1490, 1440, 1380, and 990 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}N_2OBr$: C, 53.24: H, 4.44; N, 9.56. Found: C, 53.09; H, 4.64; N, 9.71.

Alkaline Treatment of (2-Phenyl-2-oximinoethyl)triphenylphosphonium Bromide (12a).—To a solution of **12a** (9.52 g, 0.02 mole) in methanol (80 ml) was added, with stirring, a solution of potassium hydroxide (85% purity, 1.3 g, 0.02 mole) in methanol (20 ml). The crystalline precipitate was collected, washed well with water, and dried to afford a colorless product (**15a**, 7.6 g, 96%). The analytical sample was obtained by a rapid recrystallization from acetonitrile, yielding colorless needles, mp 131° dec. The nmr spectrum (100 Mc, $CDCl_3$) exhibited two multiplets at τ 2.7 and 2.4 and a doublet at 6.6 ($J_{P^{31}:H} = 12$ cps) and peak areas in the ratio of 22:2 (two multiplets, a doublet). The infrared spectrum (KBr) showed absorption bands at 3050, 2880, 1425, 1080, 1040, 1000, and 980 cm^{-1}.

Anal. Calcd for $C_{26}H_{22}NOP$: C, 78.99; H, 5.57; N, 3.54. Found: C, 78.82; H, 5.42; N, 3.70.

Analogous treatment of **12a** with triethylamine or ammonium hydroxide in place of potassium hydroxide resulted in the formation of **15a**.

In an attempt to recrystallize **15a** from benzene, a trace of yellow crystals (mp 191–192°) was isolated and found to be 2,5-diphenylpyrazine by mixture melting point determination and a comparison of infrared spectra with those of the authentic sample.[22]

Decomposition of 15a in Wet Tetrahydrofuran.—A solution of **15a** (3.95 g) in tetrahydrofuran containing water (1 ml) was refluxed for 1 hr and then concentrated. The oily residue was treated with zinc chloride in ethanol to afford the complex of triphenylphosphine oxide (2.85 g, 71%). After removal of the complex, the ethanolic solution was again concentrated and the residue was chromatographed over an unactivated alumina column. Elution with ethyl acetate yielded a brown oil, whose infrared absorption bands at 3275, 1665, 1600, 1545, 1515, 1495, 1442, 1370, 1315, 1270, 760, and 690 cm^{-1} indicated the formation of acetanilide.

Treatment of 15a with Hydrogen Chloride.—A solution of **15a** (1 g) in tetrahydrofuran (15 ml) was treated with dry hydrogen chloride under ice cooling to afford (2-phenyl-2-oximinoethyl)triphenylphosphonium chloride in a quantitative yield, which was identical, in melting point and infrared spectrum, with the product from the reaction of **13** with **2**.

Alkaline Treatment of [2-(4-Nitrophenyl)-2-oximinoethyl]triphenylphosphonium Bromide (12b).—To a suspension of **12b** (5.21 g, 0.01 mole) in methanol (150 ml) was added a solution of potassium hydroxide (85% purity, 0.65 g, 0.01 mole) in methanol (20 ml) with stirring. The mixture was filtered and the insoluble part was well washed with water and dried to afford yellow product (**15b**, 4.1 g, 93%). The analytical sample was obtained by recrystallization from ethanol, yielding yellow needles, mp 149° dec. The infrared spectrum (KBr) showed absorption bands at 3060, 1515, 1495, 1460, 1335, 1325, 1090, 1065, 1005, 1000, and 850 cm^{-1}.

Anal. Calcd for $C_{26}H_{21}N_2O_3P$: C, 70.91; H, 5.00; N, 6.36. Found: C, 71.01; H, 4.97; N, 6.72.

[2-(4-Nitrophenyl-2-benzoyloximinoethyl]triphenylphosphonium Chloride (17b).—To a suspension of **15b** (4.4 g, 0.01 mole) in pyridine (70 ml) was added dropwise a solution of benzoyl chloride (1.4 g, 0.01 mole) in benzene (10 ml) with stirring at temperature between −15 and −20° (ice–salt cooling). The mixture was stirred for 8 hr, during which the temperature was gradually raised to 15°. The insoluble product was collected by filtration, washed with benzene, and dried (5.1 g). The analytical sample was obtained by recrystallization from a small quantity of methanol as colorless needles, mp 112–113°. The infrared spectrum (KBr) showed absorption bands at 3080–2990 (br), 2930, 2850, 2780, 1745, 1520, 1435, 1350, 1250, 1110, 1060, 1030, 1005, 995, and 855 cm^{-1}.

Anal. Calcd for $C_{33}H_{26}N_2O_4PCl$: C, 68.22; H, 4.48; N, 4.82. Found: C, 68.17; H, 4.87; N, 4.98.

Registry No.—**1a**, 14181-72-7; **1b**, 14181-73-8; **1c**, 14181-74-9; **1d**, 826-94-8; **2**, 603-35-0; **9**, 1481-84-1; **11**, 14181-75-0; **12a**, 14264-66-5; **12b**, 14181-76-1; **15a** (betaine), 14181-77-2; **15a** (cyclic), 14264-70-1; **15b** (cyclic), 14181-78-3; **15b** (betaine), 14181-85-2; **16a**, 14181-79-4; **17b**, 14181-80-7; N,N′-diphenylanchoroacetamidine, 14181-81-8; (3-phenyl-3-oxo-2-oximinopropyl)triphenylphosphonium chloride, 14264-67-6; (2-phenyl-2-oximinoethyl)pyridinium bromide, 14181-82-9.

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[21] (a) H. Staudinger, *Ber.*, **44**, 537 (1911); (b) A. Reissert and A. More, *ibid.*, **39**, 3307 (1906).

[22] M. Masaki, Y. Chigira, and M. Ohta, *J. Org. Chem.*, **31**, 4143 (1966).