Polychlorinated Ketones. II. Dechlorination of Highly Chlorinated Ketones with Trivalent Phosphorus Compounds[1]

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Highly chlorinated ketones undergo rapid α,β dechlorination when treated with an equivalent amount of triphenylphosphine, triphenyl phosphite or trialkyl phosphite. Decachloro-3-pentanone (I) reacted readily with triphenylphosphine or trimethyl phosphite (molar ratio 1:2) to give 1,1,2,4,5,5-hexachloro-1,4-pentadien-3-one (II). Decachloro-2-pentanone (VI) reacted analogously with triphenyl phosphite to give a mixture of the two geometrical isomeric 1,1,1,2,3,5,5,5-octachloro-2-penten-4-ones (VIIa and VIIb). Treatment of octachlorobutanone (IX) with triphenyl phosphite or triphenylphosphine (molar ratio 1:1) afforded 1,1,2,4,4,4-hexachloro-1-buten-3-one (X). With triphenylphosphine and IX (molar ratio 2:1) an enolphosphonium salt (XI) was formed which hydrolyzed spontaneously to give 1,1,2,4,4-pentachloro-1-buten-3-one (XII). With trialkyl phosphites and IX (molar ratio 2:1) dialkyl 1,1,3,4,4-pentachloro-1,4-butadien-2-yl phosphates (XVI) are obtained in addition to dialkylphosphorochloridates (IV) and alkyl chlorides (XVII). With trialkyl phosphites and X (molar ratio 1:1) XVI and XVII were obtained.

In connection with our work on chlorinated carbonyl compounds,[1] the reaction of highly chlorinated ketones with trivalent phosphorus compounds was studied. The reaction between trialkyl phosphites and α-halo ketones (Perkow reaction) has been considerably expanded in scope since its discovery and now embraces as coreactants for the trivalent phosphorus compound a large number of compound with replaceable halogen.[4,5a] Similarly, several α,β-dichloroaldehydes react normally with trialkyl phosphites to give vinyl phosphates.[6-9]

When the reaction was extended to α,β-dibrominated carbonyl compounds, however, it was found to take a different course in that the product containing the carbonyl moiety was not a vinyl phosphate or vinyl phosphonium salt, but was instead the debrominated carbonyl compound.[10-14] To the best of our knowledge, no higher α,β-halogenated carbonyl compounds have been employed in this reaction.

Our interest in investigating the reaction of highly chlorinated ketones with trivalent phosphorus compounds was to examine the nucleophilic reactivity of triphenylphosphine, triphenyl phosphite and trialkyl phosphites and determine the nature of the reaction products. Minor changes in structure often affect the choice between competing displacements on carbon and halogen and make it difficult to predict the nature of the products.[12] Nevertheless, in the case of perchlorinated ketones, the reactions with trivalent phosphorus compounds have been found to be less complex than anticipated. For example, decachloro-3-pentanone (I) with 2 mol equiv of triphenylphosphine in ether afforded 91.2% 1,1,2,4,5,5-hexachloro-1,4-pentadien-3-one (II) in addition to dichlorotriphenylphosphorane[15] (III). Trimethyl phosphite reacted much more vigorously with I to give 95.3% II in addition to methyl chloride and dimethyl phosphorochloridate (IVa) in almost quantitative yield. 1,1,2,4,4,5,5,5-Octachloro-1-penten-3-one has been shown to be an intermediate in this reaction (see Experimental Section). In analogy to the debromination of α,β-dibromocarbonyl compounds,[11] the dechlorination of I presumably proceeds *via* a concerted E2 mechanism. S_N2 displacement of chlorine atoms was not observed. Reduction of II with sodium borohydride in aqueous ethanol afforded 1,1,2,4,5,5-hexachloro-1,4-pentadien-3-ol[16] (V).

The dechlorination of decachloro-2-pentanone (VI) with triphenyl phosphite in ether is much more sluggish, being complete after 1-hr reflux and leading to a mixture of the two geometrical isomeric 1,1,1,3,4,5,5,5-octachloro-3-penten-2-ones (VIIa and VIIb) (Scheme I) in addition to a reactive oil which appears to be dichlorotriphenoxyphosphorane (VIII) or its reaction products.[5b] The β elimination presumably involves neucleophilic attack on a positive α-chlorine atom. The *trans*-dechlorination of VI involves the conformer which is sterically more favored (eclipsed trichloroacetyl and chlorine). Because of the repulsion associated with eclipsing a trichloromethyl and trichloroacetyl group the other conformer is less favored.[17]

The reaction of octachlorobutanone (IX) with triphenyl phosphite in the presence or absence of ether was also found to give the dechlorinated product. 1,1,2,4,4,4-Hexachloro-1-buten-3-one (X) was formed in 82–96% yield. Similarly, ketone IX and triphenylphosphine afforded X and III. Ketone X is

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(1) Previous paper: K. Pilgram and H. Ohse, *J. Org. Chem.*, **34**, 1586 (1969).

(2) To whom correspondence should be addressed at the Shell Development Co.

(3) Farbenfabriken Bayer, Werk Dormagen, Germany.

(4) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961).

(5) B. Miller in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1965: (a) p 178; (b) p 143.

(6) E. C. Ladd and M. P. Harvey, U. S. Patent 2,631,162 (1949); *Chem. Abstr.*, **48**, 7048 (1954).

(7) R. R. Whetstone and D. Harman, U. S. Patent 2,765,331 (1952); *Chem. Abstr.*, **51**, 5816 (1957).

(8) W. Perkow, E. W. Krockow, and K. Knoevenagel, *Ber.*, **88**, 662 (1952).

(9) J. F. Allen and O. H. Johnson, *J. Amer. Chem. Soc.*, **77**, 2871 (1955).

(10) V. S. Abramov and N. A. Ilyina, *J. Gen. Chem. USSR*, **26**, (1956); *Chem. Abstr.*, **51**, 1822 (1957).

(11) V. S. Abramov and S. Pall, *Tr. Kazansk. Khim. Tekhnol. Inst.*, **23**, 105 (1957); *Chem. Abstr.*, **52**, 9949 (1958).

(12) S. Dershowitz and S. Proskauer, *J. Org. Chem.*, **26**, 3959 (1961).

(13) A. J. Speziale and C. C. Tung, *ibid.*, **28**, 1353 (1963).

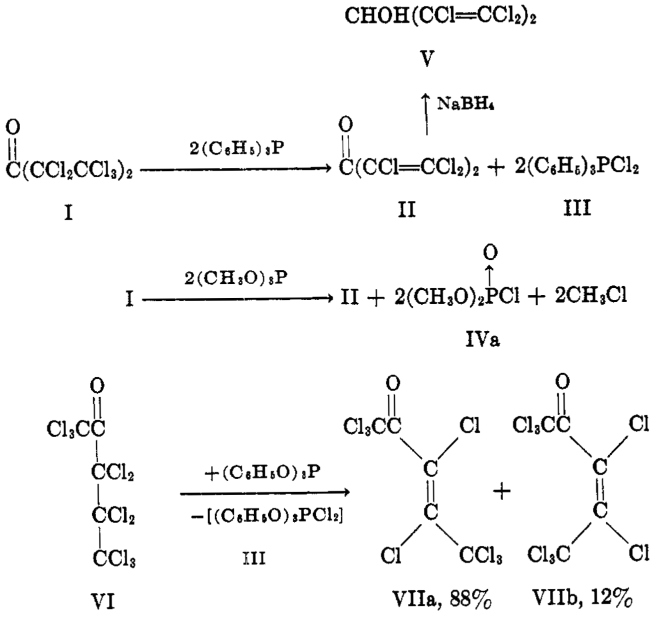
(14) C. C. Tung and A. J. Speziale, *ibid.*, **28**, 1521 (1963).

(15) The ir spectrum was identical with that of an authentic sample prepared from triphenylphosphine and chlorine. In most cases III was not isolated; it is advantageous to hydrolyse it to triphenylphosphine oxide and hydrogen chloride before isolating the dechlorinated ketone.

(16) A. Roedig and H. J. Becker, *Ber.*, **89**, 1726 (1956).

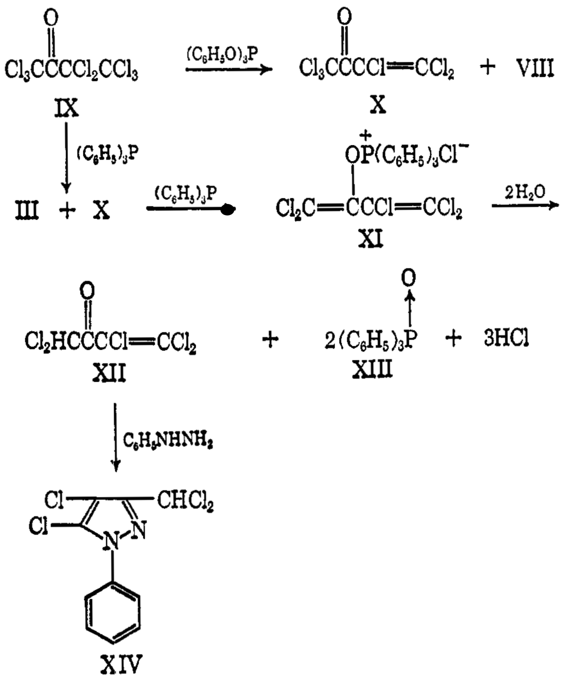
(17) M. Brown and B. W. Bremer [*J. Org. Chem.*, **32**, 1655 (1967)] have found that the nature of the elimination of bromine from vicinal dihalides by sodium selenide is a stereospecific *trans* elimination.

SCHEME I



identical with the product obtained by dehydrochlorination of 1,1,1,3,4,4,4-heptachloro-2-butanone.[1] In contrast to triphenyl phosphite which is unreactive to X,[18] 1 more mol equiv of triphenylphosphine was allowed to react with X to form vinyl phosphonium salt XI showing that triphenylphosphine is a stronger nucleophile than triphenyl phosphite (Scheme II).

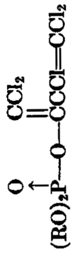
SCHEME II



Several halogenated compounds, especially α-halocarbonyl compounds which give particularly stable carbanions, are known to form quasiphosphonium salts.[19]

TABLE I

DIALKYL 1,1,3,4,4-PENTACHLORO-1,4-BUTADIEN-2-YL PHOSPHATES (XVI)



$$(RO)_2\overset{\overset{O}{\uparrow}}{P}{-}O{-}\overset{\overset{CCl_2}{\|}}{C}CCl{=}CCl_2$$

R	% yield	Bp, °C (mm)	Method of prepn	Calcd, %				Found, %			
				C	H	Cl	P	C	H	Cl	P
CH_3	95.5	85–86 (0.01)	A[a]	20.5	1.7	50.7	8.9	21.0	1.6	51.0	8.9
	76.0	88–89 (0.01)	B[b]					20.9	1.9	50.6	9.1
C_2H_5	96.8	98–99 (0.01)	A	25.4	2.6	46.5	8.2	25.6	2.8	46.6	8.0
	83.0	98–99 (0.01)	B					25.6	2.8	46.5	8.0
$CH(CH_3)_2$	94.5	99–100 (0.01)	A	29.5	3.4	43.8	7.6	31.3	4.0	42.4	8.2
	96.2	108 (0.01)	B					30.1	3.9	41.9	8.5
$CH_2CH{=}CH_2$	75.2	108–109 (0.03)	A	29.2	2.4	44.2	7.7	29.4	2.5	44.3	8.0
n-C_4H_9	74.0	121–122 (0.004)	B	33.2	4.1	40.8	7.2	33.6	4.1	40.8	7.4
n-C_5H_{11}	31.0	104–110 (0.001)	B	36.4	4.8	38.3	6.7	37.2	5.2	36.8	6.6
n-C_6H_{13}	86.0	170 (0.004)	A	39.2	5.3	36.2	6.3	40.5	5.9	33.4	6.7

[a] From X and $(RO)_3P$ (molar ratio 1:1). [b] From IX and $(RO)_3P$ (molar ratio 1:2).

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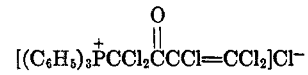
[18] On dechlorination of IX, an excess of triphenyl phosphite does not alter the yield of X.

[19] H. Hoffmann and H. J. Diehr, *Angew. Chem.*, **76**, 948 (1964); *Angew. Chem. Intern. Ed. Engl.*, **3**, 742 (1964).

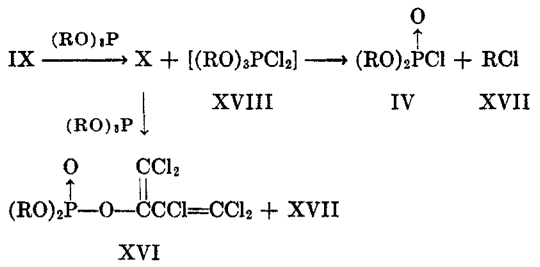
The structure of XI was proved by its quantitative conversion into 1,1,2,4,4-pentachloro-1-buten-3-one[20] (XII), triphenylphosphine oxide (XIII) and hydrogen chloride by addition of water. With phenylhydrazine and XII, the known pyrazole XIV is formed.[21] The alternate competitive reaction, formation of the β-ketophosphonium salt XV, was not observed. The


$$[(C_6H_5)_3\overset{+}{P}CCl_2\overset{\overset{O}{\|}}{C}CCl{=}CCl_2]Cl^-$$

XV

absence of salt XV that would result from SN2 displacement of chlorine we regard as supporting evidence for the postulated mechanism.[22]

Trialkyl phosphites, $(RO)_3P$, reacted exothermically with IX (molar ratio 2:1) in ether and afforded dialkyl 1,1,3,4,4-pentachloro-1,4-butadien-2-yl phosphates (XVI), dialkyl phosphorochloridates (IV) and alkyl chlorides (XVII). Reaction of X with trialkyl phosphites gave XVI directly (see Table I). Again,



the anticipated attack of phosphorus on α-chlorine occurred, followed by simultaneous elimination of chloride ion to give X and the products of a rapid Arbuzov rearrangement of XVIII. A second mole equivalent of trialkyl phosphite was allowed to react with X *via* the Perkow reaction to give eventually the vinyl phosphates XVI in addition to alkyl chlorides (XVII).

Experimental Section

Melting points were taken in capillary tubes. They as well as boiling points are uncorrected. Gas chromatograms were recorded on a Model 500 linear programmed temperature gas chromatograph (F & M Scientific Corp., Avondale, Pa.). Nuclear magnetic resonance spectra were obtained on a KIS-2, 90-Mcps spectrometer, using hexadeuterioacetone as solvent and TMS as internal standard. Ultraviolet spectra were obtained in methanol with a Cary 14 spectrophotometer (200–350 mμ). Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

Materials.—Triphenylphosphine, triphenylphosphite, and trimethyl- and triethylphosphite were obtained commercially and recrystallized or redistilled before use. Triallyl, triisopropyl, tributyl, triamyl, and trihexyl phosphite were prepared from the corresponding alcohols and phosphorus trichloride in the presence of N,N-dimethyl- or -diethylaniline in ether according to published methods.

Dechlorination of Decachloro-3-pentanone (I). A. With Triphenylphosphine.—To a stirred solution (22°) of 86.2 g (0.2 mol) of I[23] in 200 ml of ether was added gradually a solution of 104.8 g (0.4 mol) of triphenylphosphine in 1000 ml of ether. The reaction was exothermic and the temperature rose to 35°. An ir spectrum indicated the mixture to contain II and III. After the reaction mixture was allowed to cool to room temperature, 500 ml of water was added dropwise with stirring. (*Caution:* during addition of the first milliliter of water, the reaction is vigorous.) Most of the triphenylphosphine oxide precipitated and was removed by filtration. The ether solution was dried ($CaCl_2$) and evaporated to dryness. The yellow residual oil was purified by distillation under vacuum to give 52.2 g (91.2%) of 1,1,2,4,5,5-hexachloro-1,4-pentadien-3-one (II): bp 69° (0.3 mm) [lit.[16] bp 94–95° (0.6 mm)]; $n^{20}D$ 1.5661; d^{20}_4 1.6963; ir (thin film) 5.73 (C=O) and 6.3 μ (C=C).

Anal. Calcd for C_5Cl_6O: C, 20.8; H, 0.0; Cl, 73.7. Found: C, 21.1; H, 0.2; Cl, 73.9.

B. With Trimethyl Phosphite.—Trimethyl phosphite, 49.6 g (0.4 mol), was dissolved in 50 ml of ether and then added dropwise with stirring to I, 86.2 g (0.2 mol), in 200 ml of ether. The reaction was vigorous and the flask was cooled with ice water. Methyl chloride was condensed in a cold trap. After 0.2 mol of trimethyl phosphite had been added, the reaction mixture contained dimethyl phosphorochloridate (IVa) and the following ketones: I (17.5%), 1,1,2,4,4,5,5,5-octachloro-1-penten-3-one (62.8%), identified by glpc comparison with an authentic sample,[16] and II (19.7%). After the second portion of trimethyl phosphite had been added, only II and IVa were detected by glpc. The cold trap contained 24.7 g (95%) of methyl chloride. Ether was removed from the reaction mixture and the products were separated by distillation under vacuum to give 57.6 g (99.6%) of dimethyl phosphorochloridate (IVa): bp 60° (8 mm); $n^{20}D$ 1.4184.

Anal. Calcd for $C_2H_6ClO_3P$: Cl, 24.6; P, 21.4. Found: Cl, 25.8; P, 20.5.

The second fraction distilled at 66° (0.005 mm) and afforded 55.1 g (95.3%) of II as light yellow oil which was identical with the product obtained in A.

1,1,2,4,5,5-Hexachloro-1,4-pentadien-3-ol (V).—To a solution of sodium borohydride, 1.0 g, in 80 ml of water and 20 ml of ethanol was added dropwise with stirring a solution of 28.9 g of II in 20 ml of ethanol. The flask was cooled with ice water during the addition. After 1 hr, 250 ml of water was added and the reaction mixture was thoroughly extracted with ether. The combined extractions were dried (Na_2SO_4) and evaporated to dryness. The residue, 29.0 g, was recrystallized from petroleum ether (bp 30–60°) to give 13.0 g (44.7%) of 1,1,2,4,5,5-hexachloro-1,4-pentadien-3-ol (V) as white crystalline solid, mp 53–53.5° (lit.[16] mp 53–53.5°).

Anal. Calcd for $C_5H_2Cl_6O$: C, 20.7; H, 0.7; Cl, 73.2. Found: C, 20.6; H, 0.9; Cl, 73.1.

Dechlorination of Decachloro-2-pentanone (VI).—To a solution of 129.3 g (0.3 mol) of VI in 100 ml of ether was added 93.0 g (0.3 mol) of triphenyl phosphite dissolved in 50 ml of ether. The mixture was heated to reflux for 1 hr. Ether was removed and the residual oil was distilled under vacuum at 90–120° (1–0.1 mm) to give 80 g of a crude material which was redistilled at 88–89° (0.05 mm) to give 73.0 g (67.6%) of 1,1,1,3,4,5,5,5-octachloro-3-penten-2-one (VIIa + VIIb). Glpc indicated a mixture of two compounds in a ratio of 88:12. The ir spectrum indicated the absence of CH bands and showed strong absorption at 1750 (C=O) and 1595 cm^{-1} (C=C).

Anal. Calcd for C_5Cl_8O: Cl, 78.9. Found: Cl, 78.6.

Dechlorination of Octachlorobutanone (IX). A. With Triphenyl Phosphite in Ether.—To a solution of IX, 174 g (0.5 mol), in 400 ml of ether was added dropwise with stirring triphenyl phosphite, 155 g (0.5 mol). Exothermicity was not observed, but the color of the solution changed to a grayish green. The solvent was removed under vacuum and the reaction mixture was distilled through a 30-cm Vigreux column. The temperature of the oil bath was gradually raised to 130° and the fraction at 40–50° (0.2 mm), 140 g, was redistilled at 44° (0.2 mm) to give 114 g (82.3%) of 1,1,2,4,4,4-hexachloro-1-buten-3-one (X): $n^{20}D$ 1.5321; ir (thin film) 1745 (C=O) and 1585 cm^{-1} (C=C); uv max 205 mμ (ε 7139) and 245 (7430).

Anal. Calcd for C_4Cl_6O: Cl, 76.9. Found: Cl, 76.8.

The residue which contained dichlorotriphenoxyphosphorane (VIII) or its reaction products[5b] solidified in the flask and was readily soluble in water.

B. Without Ether.—When triphenyl phosphite, 310 g (1.0 mol), and 174 g (0.5 mol) of IX were mixed at 22°, the temperature rose briefly to 40°. The mixture was immediately dis-

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[20] The preparation of XII by acid-catalyzed thermolysis of the corresponding di(*sec*-butyl)vinyl phosphate analogous to XVI has been described recently: K. Pilgram and H. Ohse, *Angew. Chem.*, **78**, 820 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 836 (1966).

[21] A. Roedig and H. J. Becker, *Ann.*, **597**, 214 (1956).

[22] Vinylphosphonium salts are extremely sensitive to solvolytic reagents and decompose with water to give α-monodehalogenated carbonyl compounds whereas β-ketophosphonium salts are stable under neutral and acidic conditions.[19]

[23] M. Geiger, E. Usteri, and Ch. Gränacher, *Helv. Chim. Acta.*, **34**, 1340 (1951).

tilled under vacuum. The temperature of the oil bath was gradually raised to 160°. A forerun, 20 g, bp 39° (0.15 mm), was followed by the main fraction which afforded 132.7 g (96.3%) of X: bp 42–44° (0.15 mm); n^{20}_{D} 1.5324. The ir spectrum was superimposable with that of X, obtained above.

C. With Triphenylphosphine in Ether.—A solution of IX, 34.8 g (0.1 mol), in 50 ml of ether was added dropwise with stirring to a solution of triphenylphosphine, 52.4 g (0.2 mol), in 1000 ml of ether at 25–35°. After the addition was complete, no starting material could be detected in solution by means of glpc. Water, 500 ml, was added dropwise with stirring. Triphenylphosphine oxide precipitated out shortly afterward and was removed by suction-filtration. The ether layer was dried ($CaCl_2$) and evaporated to dryness. The crude product was purified by distillation to give 39.8 g (82.1%) of 1,1,2,4,4-pentachloro-1-buten-3-one (XII): bp 89° (9 mm); n^{20}_{D} 1.5440; d^{20}_{4} 1.6628 [lit.[24] bp 99–100° (13 mm); n^{20}_{D} 1.4442]; ir (film) 5.9 (C=O) and 6.5 μ (C=O); uv max 212 mμ (ε 7953) and 271 (3071); nmr δ 6.76.

Anal. Calcd for C_4HCl_5O: C, 19.8; H, 0.4; Cl, 73.2. Found: C, 20.0; H, 0.7; Cl, 73.2.

1-Phenyl-4,5-dichloro-3-dichloromethylpyrazole (XIV).—To a solution of 24.25 g (0.1 mol) of XII in 300 ml of ether was added dropwise a solution of 21.6 g (0.2 mol) of phenylhydrazine in 50 ml of ether. After 30 min 200 ml of water was added. The organic layer was dried (Na_2SO_4) and evaporated to dryness. The crude pyrazole was purified by distillation under vacuum to give 12.43 g (42%) of pure XIV, which solidified: bp 142° (0.4 mm); mp 55–55.5° [lit.[21] mp 57.5–58°; bp 155° (0.8 mm)]; uv max 247 mμ (ε 11,566); nmr δ 7.00 (aliphatic H) and 7.45 (aromatic H).

Anal. Calcd for $C_{10}H_6Cl_4N_2$: C, 40.5; H, 2.0; Cl, 47.9; N, 9.5. Found: C, 40.4; H, 2.2; Cl, 47.5; N, 9.7.

Reaction of Octachlorobutanone (IX) and 1,1,2,4,4,4-Hexachloro-1-buten-3-one (X) with Trialkyl Phosphites.—The results are summarized in Table I. The general procedures are illustrated by the reactions of IX and X with trimethyl phosphite.

A.—To a stirred solution of IX, 34.8 g (0.1 mol), in 50 ml of ether was added dropwise trimethyl phosphite, 24.8 g (0.2 mol). The reaction was exothermic and the ether started to boil. The reaction mixture was heated to reflux for 10 min. Ether was removed under vacuum and the residual oil was distilled to give 13.0 g (90%) of dimethyl phosphorochloridate (IVa), bp 60–62° (8 mm), identical (glpc) with the product obtained by dechlorination of I with trimethyl phosphite (see above). The vinyl phosphate XVI ($R = CH_3$) distilled at 88–89° (0.01 mm): 26.6 g (76%); n^{20}_{D} 1.5173; d^{20}_{4} 1.5869. The ester is a colorless liquid and turns light yellow on storage for several weeks when exposed to sunlight: uv max 208 mμ (ε 20,088) and max 247 (7375); ir (film) 6.35 (C=C) and 7.7 μ (P→O).

B.—To a stirred solution of X, 10.65 g (0.0385 mol) in 20 ml of ether, was added trimethyl phosphite, 6.2 g (0.05 mol), dissolved in 20 ml of ether. The reaction was exothermic. Ether was removed and the residual oil was purified by distillation to give 12.9 g (95.5%) of XVI ($R = CH_3$): n^{20}_{D} 1.5163; d^{20}_{4} 1.5899; uv and ir spectrum were identical with the product obtained in A.

Registry No.—II, 13340-09-5; IVa, 813-77-4; V, 18791-16-7; VIIa, 18766-86-4; VIIb, 18791-17-8; X, 13340-11-9; XII, 13340-10-8; XIV, 18767-09-4; XVI (R = Me), 18767-10-7; XVI ($R = C_2H_5$), 18767-11-8; XVI [$R = CH(CH_3)_2$], 18767-12-9; XVI ($R = CH_2CH{=}CH_2$), 18767-13-0; XVI ($R = n\text{-}C_4H_9$), 18767-14-1; XVI ($R = n\text{-}C_5H_{11}$), 18767-15-2; XVI ($R = n\text{-}C_6H_{13}$), 18791-18-9.

[24] A. Roedig and H. J. Becker, *Ber.*, **89**, 906 (1956).

The Reactions of Triphenylphosphine with α-Halobenzyl Phenyl Ketones and with α-Mesyloxybenzyl Phenyl Ketone[1]

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The reactions of α-bromobenzyl phenyl ketone (**11**) and α-chlorobenzyl phenyl ketone (**14**) with triphenylphosphine are described. Both enol phosphonium and ketophosphonium halides are formed in ratios dependent upon reaction conditions. The enol phosphonium halides are solvolyzed to deoxybenzoin (**16**) and converted into diphenylacetylene (**17**). Debromination of **11** to **16** occurs with triphenylphosphine in the presence of methanol. α-Mesyloxybenzyl phenyl ketone (**19**) reacts with triphenylphosphine to give only the α-ketophosphonium mesylate *via* displacement of mesylate ion. Probable mechanisms for the observed reactions and the relationships of these reactions to the reactions of other α-halo ketones with phosphines are discussed.

Recent work has shown that the reactions of triphenylphosphine with α-bromoacetophenone (**1**) and with α-bromopropiophenone (**2**) give the corresponding α-ketotriphenylphosphonium bromides in aprotic solvents.[3,4] Our kinetic studies indicate that both **1** and **2** probably react with triphenylphosphine *via* displacement of bromide ion under aprotic conditions.[5,6]

We and others have previously postulated that the reactions of certain α-halo ketones such as 2-bromodimedone and the α-halobenzyl phenyl ketones (desyl halides) with triphenylphosphine can involve the formation of enol phosphonium salts.[7,8] Enol phosphonium salts including **7–10** have been isolated from the reaction of triphenylphosphine with chlorobenzhydryl phenyl ketone **3**,[9] the corresponding bromo ketone **4**,[10a] dibromobenzyl phenyl ketone **5**,[10b] dibromopropiophenone (**6**), and from other α-dihalo ketones[10a] (Scheme I).

It has been suggested that enol phosphonium salts may arise *via* displacement by triphenylphosphine on halogen of an α-halo ketone to give an enolate halotri-

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[3] (a) I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963); (b) I. J. Borowitz, K. C. Kirby, Jr., and R. Virkhaus, *J. Org. Chem.*, **31**, 4031 (1966).

[4] (a) F. Ramirez and S. Dershowitz, *ibid.*, **22**, 41 (1957); (b) A. V. Dombrovskii and M. I. Shevchuk, *Zh. Obshch. Khim.*, **33**, 1263 (1963).

[5] I. J. Borowitz and H. Parnes, *J. Org. Chem.*, **32**, 3560 (1967).

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