Polychlorinated Ketones. III. Formation by Acid-Catalyzed Cleavage of Vinyl Phosphates and Phosphonates[1]

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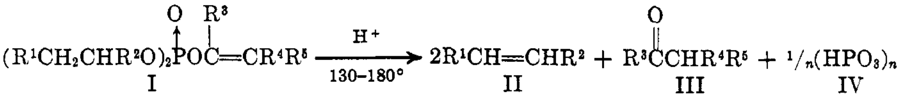
Alkenyl di-*sec*-alkyl phosphates (I) are cleaved at 130–180° in the presence of catalytic amounts ($\leqslant 0.5\%$) of concentrated sulfuric or *p*-toluenesulfonic acid to alkenes (II), carbonyl compounds (III), and polymetaphosphoric acid (IV). A carbonium ion mechanism is proposed for the formation of II. The formation of III presumably involves an ionic type cleavage. With the availability of chlorocarbonyl compounds of general structure $R^3C(=O)CClR^4R^5$, a great variety of new mono-α-dechlorinated carbonyl compounds, III, can now conveniently be prepared.



$$\underset{\text{I}}{(R^1CH_2CHR^2O)_2\overset{\overset{O}{\uparrow}}{P}O\overset{\overset{R^3}{|}}{C}{=}CR^4R^5} \xrightarrow[130-180^\circ]{H^+} \underset{\text{II}}{2R^1CH{=}CHR^2} + \underset{\text{III}}{R^3\overset{\overset{O}{\|}}{C}CHR^4R^5} + \underset{\text{IV}}{{}^1/_n(HPO_3)_n}$$

Although hydrolysis, alcoholysis, and acidolysis of vinyl phosphates have been known for many years,[4] they have little synthetic utility for the preparation of carbonyl compounds and are more useful as a degradation process to confirm the structures of many vinyl phosphates. Pyrolysis of organophosphorus compounds involving elimination reactions to give olefins in preparative yield has become available only recently.[5]

In the present work we wish to demonstrate that acid-catalyzed cleavage of di-*sec*-alkyl vinyl phosphates is a useful preparative method for selective mono-α-dechlorination of chlorocarbonyl compounds used originally in the preparation of the vinyl phosphates. The main compounds chosen for this study were obtained by reaction of polychlorinated butanones and butenones with trialkyl phosphites, reported in our previous paper.[1]

Results and Disucssion

A series of 14 vinyl phosphates (**1–14**) and one phosphonate (**15**) were prepared by reaction of an α-chlorocarbonyl compound with the respective trialkyl phosphite and phenyl diisopropyl phosphonite (Perkow reaction). The compounds thus prepared are listed in Table I. Of these products, **9**[6,7] and **10**[6] have been described in the literature. In two instances (**8** and **12**), the esters decomposed on attempted distillation under vacuum (0.01 mm). With these exceptions, all esters in Table I proved to be stable when heated at 180° for 2 hr.

Thermal degradation of esters **1–15** was carried out at atmospheric pressure in the presence of catalytic amounts (0.01–0.1 mol %) of concentrated sulfuric acid or *p*-toluenesulfonic acid. A thermometer placed in the reaction medium permitted the temperature to be observed throughout the thermolysis. Temperature ranges within which thermal degradation proceeded smoothly are given in Table II. Concentrated sulfuric and *p*-toluenesulfonic acid proved to be more effective catalysts than 85% phosphoric acid.[8]

The volatile olefin was collected in a cold trap; the yield in all runs was essentially quantitative. The course of the thermolysis, which was completed within 1 to 2 hr, could be followed visually, since the vigorous gas evolution ceased at the end of the reaction. The carbonyl compounds were isolated from the dark-colored residual oils by distillation (**9–15**). In two experiments (**7** and **8**), the ketones were obtained by crystallization techniques. In one instance (**10**), the carbonyl compound was not isolated; since it is thermally unstable, the chloroacetaldehyde formed by decomposition of **10** was trapped and immediately reacted in the receiver with triethyl phosphite to give diethyl vinyl phosphate. Proof of structure experiments described in the Experimental Section provide additional evidence for the proposed structures of the degradation products.

Interestingly, the esters **1–6** were relatively stable when heated at 170–180° in the presence of catalytic amounts of concentrated sulfuric acid over a period of 2 hr. For example, ester **1** and **2** produced only traces of 1,1,4,4-tetrachloro-1-buten-3-one. Analysis of the pyrolysate of esters **3–6** indicated only 5–10% of the anticipated olefin and ketone in addition to unreacted ester. However, cleavage of esters **7–15** proceeded smoothly at 160–180° in the presence of traces of concentrated sulfuric acid. Thus, the tendency of a dialkyl vinyl phosphate, $(RO)_2P(O)O\overset{|}{C}{=}C{<}$, to undergo acid-catalyzed thermal degradation is determined primarily by the nature of the alkyl group and increases in the following order of R.

$$CH_3,\ C_2H_5 < C_3H_7,\ C_4H_9,\ C_5H_{11},\ C_6H_{13} \ll CH(CH_3)_2,\ CH(CH_3)CH_2CH_3$$

The possibility arises that this cleavage (to give olefin) may proceed either by an E1 (unimolecular) or an intramolecular (*cis*) elimination.[9,10] The order of reac-

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[1] Previous paper: K. Pilgram and H. Ohse, *J. Org. Chem.*, **34**, 1592 (1969). Published, in part, in *Angew. Chem.*, **78**, 820 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 836 (1966).

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[4] For lead references, see F. W. Lichtenthaler, *Chem. Rev.*, **61**, 624–628 (1961).

[5] For lead references, see (a) H. E. Baumgarten and R. S. Setterquist, *J. Amer. Chem. Soc.*, **79**, 2605 (1957); (b) K. D. Berlin and T. H. Austin, *J. Org. Chem.*, **30**, 2745 (1965).

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

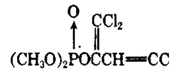
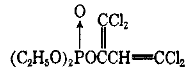
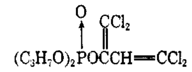
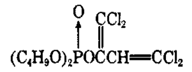
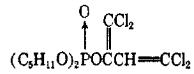
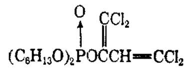
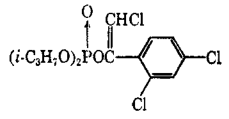
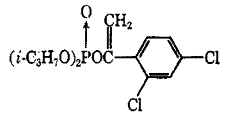
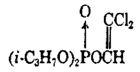
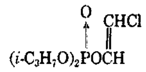
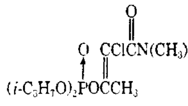
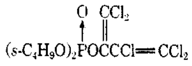
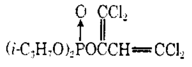
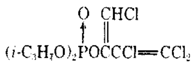
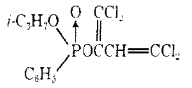
[7] W. Perkow, *Ber.*, **87**, 755 (1954).

[8] The referee has suggested that phosphoric acid is not an effective catalyst, because it might react with VII, forming an anhydride, and thereby prevent its conversion to VIII.

[9] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[10] E. S. Gould in "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., New York, N. Y., 1959.

TABLE I
VINYL ESTERS

Compd	Structure	Yield, %	Bp, °C (mm Hg) (or mp, °C)	Analyses, % C Calcd	C Found	H Calcd	H Found	Cl Calcd	Cl Found	P Calcd	P Found
1	 $(CH_3O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	78.0	91–92 (0.001)	22.8	23.3	2.2	2.4	45.0	45.9	9.8	9.2
2	 $(C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	88.5	97–98 (0.07)	27.9	28.1	3.2	3.2	41.3	40.8	9.0	9.1
3	 $(C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	74.0	99–100 (0.01)	33.2	33.3	4.0	4.2	38.2	37.5	8.3	8.6
4	 $(C_4H_9O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	68.0	121 (0.008)	36.0	36.6	4.7	4.7	35.5	35.5	7.8	7.8
5	 $(C_5H_{11}O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	63.6	136 (0.005)	39.2	41.5	5.4	5.7	33.2	33.2	7.2	7.5
6	 $(C_6H_{13}O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	64.5	160–163 (0.005)	42.1	42.0	5.9	6.2	31.1	31.3	6.8	6.8
7		57.4	(31)	43.4	43.6	4.7	4.8	27.4	27.7	8.0	8.0
8		Crude[a]									
9	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}H$	86.5	73–74 (0.001)	34.7	35.1	5.4	5.5	25.6	24.7	11.2	10.9
10	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CHCl}{\overset{\|}{C}}H$	77.0	49–50 (0.001)	39.7	39.2	6.6	6.7	14.6	14.4	12.8	12.9
11	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl\overset{O}{\overset{\|}{C}}N(CH_3)_2}{\overset{\|}{C}}CH_3$	68.6	132–134 (0.01)	44.0	44.2	7.0	7.3	10.8	10.3	9.5	9.1
12	 $(s\text{-}C_4H_9O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CCl{=}CCl_2$	Crude[a]									
13	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CCl_2}{\overset{\|}{C}}CH{=}CCl_2$	75.8	94–95 (0.005)	32.3	32.8	4.0	4.2	38.2	37.6	8.3	8.5
14	 $(i\text{-}C_3H_7O)_2\overset{O}{\overset{\uparrow}{P}}O\overset{CHCl}{\overset{\|}{C}}CCl{=}CCl_2$	90.0	124–125 (0.05)	...	...	...	...	38.2	38.5	8.3	8.2
15		73.0	170–180 (0.008)	40.0	39.7	3.3	3.5	36.4	37.2	8.0	8.3

[a] Reaction product was not analyzed; distillation was attempted but decomposition occurred.

tivity, primary < secondary, clearly is that which would be anticipated for a reaction involving a carbonium-ion intermediate (E1). This is also most certainly the route by which acid-catalyzed dehydrations of most alcohols proceed.[10] Initial protonation (E1 reaction) may be envisaged to involve the phosphoryl-oxygen atom (Va) or the oxygen atom of the alkoxy group (Vb) followed by elimination of a proton from the β-carbon atom of the intermediate carbonium ion (VI) (see Scheme I). A contributing factor to the intermediate Va would be the greater basicity of the phosphoryl-oxygen atom compared with the oxygen atom of the alkoxy group. If R^6 represents a secondary alkoxy group, then a second mole equivalent of olefin II is eliminated from VII *via* similar "onium" intermediates before formation of carbonyl compound III takes place.

Although a concerted mechanism involving the cyclic transition state VIII (intramolecular elimination) can be written for cleavage of VII to give III which resembles that generally accepted for the pyrolysis of alkyl carboxylates containing a β-hydrogen atom,[9] there is qualitative evidence that this cleavage is also acid catalyzed and may well proceed *via* an ionic intermediate IX, either to the exclusion of or in competition with the cyclic mechanism VIII.[11] For example, the

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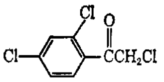
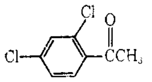
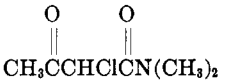
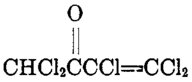
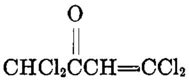
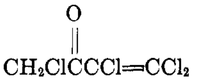
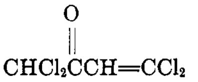
(11) Protonation of the phosphoryl-oxygen atom in VII is very likely to take place also, but would give an intermediate which could not give the observed product.

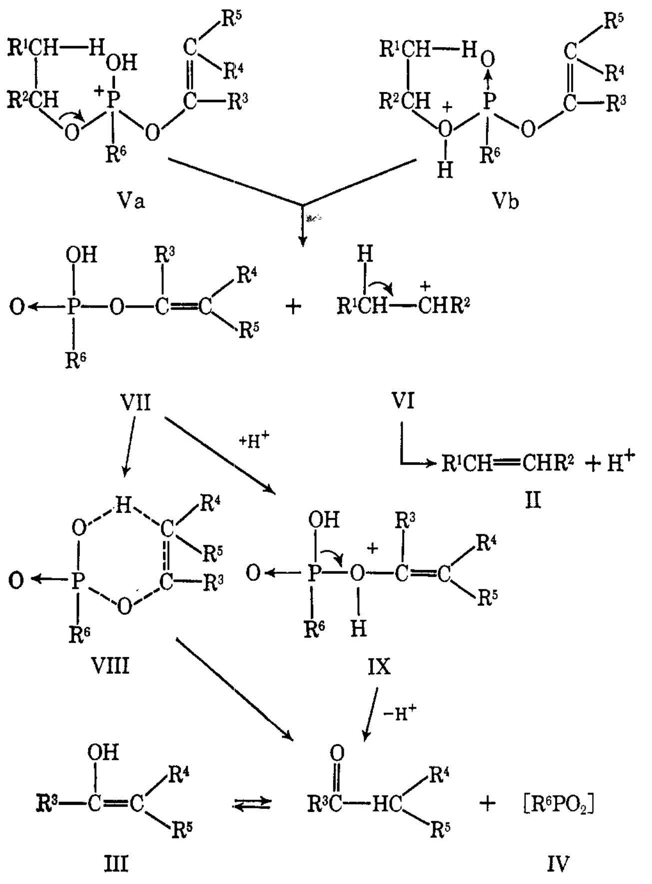
TABLE II

DECOMPOSITION DATA OF VINYL PHOSPHATES

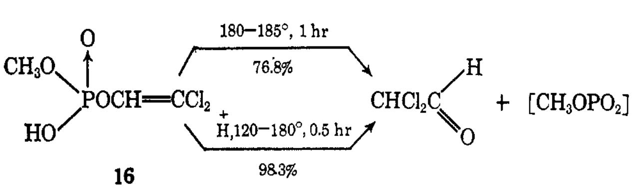
	Decomposition			Carbonyl compound isolated				Analyses, %					
								C		H		Cl	
Ester	Temp, °C	Time, hr	Catalyst	Yield, %	Structure	Registry no.	Bp, °C (mm) (or mp, °C)	Calcd	Found	Calcd	Found	Calcd	Found
7	165	1	*p*-TSA[a]	95.3		4252-78-2	(54.5)[b]	43.0	43.0	2.2	2.7	47.5	47.7
7	165	1	H_2SO_4	87.2									
8	165	1.4	H_2SO_4	36.7		2234-16-4	(29–31)[c]	50.8	50.7	3.2	3.3	37.6	37.7
9	150–160[d]	1	H_2SO_4	79	$CHCl_2CHO$	79-02-7	84–86 (760)[e]	...	...	...	...	62.8	62.5
16	180–185	1	*f*	76.8	$CHCl_2CHO$		84–86 (760)	...	...	...	...	...	...
16	120–180	0.5	H_2SO_4	98.3	$CHCl_2CHO$		84–86 (760)	...	...	...	...	...	...
10	160	1	H_2SO_4	33.3	CH_2ClCHO[g]		...	...	...	...	...	...	...
11	150	1.5	*p*-TSA	73.7	 $CH_3\overset{O}{\overset{\|}{C}}CHCl\overset{O}{\overset{\|}{C}}N(CH_3)_2$	5810-11-7	60–61 (0.001)[h]	44.0	44.0	6.1	6.2	21.7	21.2
12	165–170	1	H_2SO_4	96.3	 $CHCl_2\overset{O}{\overset{\|}{C}}CCl{=}CCl_2$	13340-10-8	87–88 (10)[i]	19.3	20.0	0.4	0.7	73.2	73.2
13	130–165	1.5	H_2SO_4	74.5	 $CHCl_2\overset{O}{\overset{\|}{C}}CH{=}CCl_2$	10561-99-6	77 (10)	23.1	23.4	1.0	1.2	68.3	67.8
14	155–165	1.5	H_2SO_4	86.6	 $CH_2Cl\overset{O}{\overset{\|}{C}}CCl{=}CCl_2$	21555-32-1	46–47 (0.02)[j]	...	...	...	...	68.3	68.8
15	180	1.5	H_2SO_4	72.0	 $CHCl_2\overset{O}{\overset{\|}{C}}CH{=}CCl_2$		72–73 (9)[k]	23.1	23.2	1.0	1.3	68.3	68.0

[a] *p*-Toluenesulfonic acid. [b] From methanol. [c] From methanol–hexane (1:1). [d] At 100 mm. [e] n^{20}_D 1.4625. [f] Uncatalyzed. [g] Identified as diethyl vinyl phosphate. [h] n^{20}_D 1.4860; nmr (CCl_4) δ 2.26 (CH_3), 5.41 (CHCl), 3.16 and 2.95 [$N(CH_3)_2$]. [i] n^{20}_D 1.5421; d^{20} 1.6643; nmr (CCl_4) δ 6.76. [j] n^{18}_D 1.5386; nmr (CCl_4) δ 4.5 (CH_2Cl). [k] n^{20}_D 1.5371; d^{20} 1.5736; nmr (CCl_4) δ 5.96 ($CHCl_2$), 7.15 (CH=).

SCHEME I



amount of dichloroacetaldehyde formed by "self-decomposition" of 2,2-dichlorovinyl methyl phosphoric acid (**16**) was considerably smaller (76.8%) and required a higher reaction temperature (180–185°) and longer reaction time (1 hr) than the acid-catalyzed degradation of **16**. The latter proceeded with a measurable rate already at 120° and was completed within 30 min after the reaction temperature had been raised to 180°, giving dichloroaceteldehyde in almost quantitative yield.



We have demonstrated that this facile acid-catalyzed thermolysis of suitably constituted vinyl phosphates and phosphonates represents a convenient preparative method for the selective mono-α-dechlorination of chlorocarbonyl compounds originally used in the preparation of the vinyl phosphates and phosphonates. With the availability of chlorocarbonyl compounds of general structure $R^1C({=}O)CH_mCl_nR^2$, a variety of new carbonyl compounds, $R^1C({=}O)CH_{m+1}Cl_{n-1}R^2$, can now be prepared *via* these Perkow intermediates. This complements the other syntheses of α-chlorinated carbonyl compounds using a variety of chlorination techniques.[12]

Experimental Section

Materials.—The trialkyl phosphites were prepared from the appropriate alcohol and phosphorus trichloride in ether and in the presence of N,N-diethylaniline. Diisopropyl phenyl phosphonite was prepared analogously from 2-propanol and phenyl dichlorophosphine. 1,1,4,4,4-pentachloro-1-buten-3-one,[13] 1,1,2,-4,4,4-hexachloro-1-buten-3-one,[13] 2,2,2′,4′-tetrachloroacetophenone,[14] and N,N-dimethyl-2,2-dichloroacetoacetoamide[15] were each prepared according to a literature procedure. 2-Chlorovinyl diisopropyl phosphate and 2,2-dichlorovinyl diisopropyl phosphate were prepared as previously described.[6,7] The latter procedure was also used to prepare the new vinyl phosphates summarized in Table I.

Cleavage of Diisopropyl 2-Chloro-1-(2,4-dichlorophenyl)vinyl Phosphate (7). A. In the Presence of *p*-Toluenesulfonic Acid.—A 100-ml, two-necked reaction flask equipped with magnetic stirrer, internal thermometer, and reflux condenser connected with a cold trap was charged with 19.38 g (0.05 mol) of **7** and 0.2 g of *p*-toluenesulfonic acid. The temperature was gradually raised (oil bath) with stirring. The evolution of gas became very vigorous at 165° and had ceased after 1 hr. The reaction mixture was cooled and recrystallized (CH_3OH) to give 10.65 g (95.3%) of 2,2′,4′-trichloroacetophenone, mp 54.5° (lit.[16] mp 57°). The cold trap contained 4.1 g (97.7%) of propene, which was identified by mass spectroscopy (*m/e* 42) and by its quantitative conversion to 1,2-dibromopropane with bromine: bp 139–141° (lit.[17] bp 139–142°).

Anal. Calcd for $C_3H_6Br_2$ (mol wt 201.9): Br, 79.2. Found: Br, 79.0.

B. In the Presence of Sulfuric Acid.—Triisopropyl phosphite (44 g, 0.211 mol) was treated with 2,2,2′,4′-tetrachloroacetophenone (50 g, 0.194 mol) in 30 ml of ether to give **7**. After all volatile products had been removed at 60° (20 mm), 0.2 ml of concentrated sulfuric acid was added to the crude ester **7** and the mixture was gradually heated with stirring in an oil bath to 165°. After 1 hr, the evolution of propene had ceased for all practical purposes. Recrystallization from hexane afforded 37.8 g (87.2%) of 2,2′,4′-trichloroacetophenone, mp 54.5°.

C. In the Presence of 85% Phosphoric Acid.—When 85% phosphoric acid was used in an analogous experiment, it was observed that the generation of propene came to a complete standstill shortly after the temperature had reached 165°. When more phosphoric acid was added, propene was generated for another brief period of time only. In addition, water had collected in the receiver, presumably owing to dehydration of phosphoric acid.[8]

Cleavage of Diisopropyl 1-(2,4-Dichlorophenyl)vinyl Phosphate (8).—Triisopropyl phosphite (45 g, 0.216 mol) was added dropwise with stirring to a solution of 2,2′,4′-trichloroacetophenone in 100 ml of ether. After completion of the exothermic reaction, ether and isopropyl chloride were removed *in vacuo*. Attempts to crystallize ester **8** failed, and attempted purification by distillation *in vacuo* lead to decomposition. Therefore, concentrated sulfuric acid (0.1 ml) was added and the reaction mixture was heated at 165° until evolution of propene had stopped (85 min). Subsequent recrystallization from hexane and methanol with the aid of charcoal afforded 14.55 g (36.7%) of 2,4-dichloroacetophenone as a colorless crystalline solid, mp 29–31° (lit.[18] mp 33–34°). Analysis by glpc of the mother liquors indicated more 2,4-dichloroacetophenone.

Cleavage of Diisopropyl 2-Chlorovinyl Phosphate (10).—A mixture of 36.4 g (0.15 mol) of **10** and 0.1 ml of concentrated sulfuric acid was heated with stirring in an oil bath at 160°. Propene and chloroacetaldehyde were trapped in a cold trap which contained 24.9 g of triethyl phosphite. At the end of the reaction, the residue exploded violently. The contents of the receiver were gradually heated to 90°. Excess phosphite was removed and fractional distillation of the residual liquid gave 9.0 g (33.3%) of diethyl vinyl phosphate, bp 52° (0.005 mm), $n^{20}{}_D$ 1.4130. This technique was used because of the thermal instability of chloroacetaldehyde.

Anal. Calcd for $C_6H_{13}O_4P$ (mol wt 180.2): C, 40.0; H, 7.2; P, 17.2. Found: C, 40.0; H, 7.5; P, 16.8.

1,1,3,4,4,4-Hexachlorobutan-2-one.—Chlorine was passed into 1,1,4,4-tetrachloro-1-buten-3-one (20.8 g, 0.1 mol) under irradiation with ultraviolet light at 0°. After 1.5 hr, the crude product (26.2 g, 93.9%) was distilled to give 19.7 g (70.7%) of 1,1,3,4,4,4-hexachlorobutan-2-one: bp 105–107° (9 mm); $n^{20}{}_D$ 1.5222, d^{20} 1.7019; nmr (CCl_4) δ 5.52 (CHCl) and 6.48 ($CHCl_2$).

Anal. Calcd for $C_4H_2Cl_6O$ (mol wt 278.8): C, 17.2; H, 0.7; Cl, 76.4. Found: C, 17.8; H, 1.0; Cl, 76.8.

Dimethyl 3,4,4-Trichloro-1,3-butadien-2-yl Phosphate.—To a solution of 20.8 g (0.1 mol) of 1,1,2,4-tetrachloro-1-buten-3-one in 50 ml of ether was added dropwise with stirring 24.8 g (0.2 mol) of trimethyl phosphite dissolved in 25 ml of ether. The reaction was exothermic. Distillation afforded 21.0 g (74.7%) of the ester: bp 100–101° (0.03 mm); $n^{18}{}_D$ 1.4938; ir main bands at 1647 and 1581 (C=C), 1300 + 1285 ($P \rightarrow O$), and 1045 cm^{-1} (POC); nmr (CCl_4) δ 3.8 (OCH_3), 5.2, and 5.5 ($=CH_2$).

Anal. Calcd for $C_6H_8Cl_3O_4P$ (mol wt 281.5): Cl, 37.9; P, 11.0. Found: Cl, 37.6; P, 11.0.

Registry No.—**1,** 21555-24-8; **2,** 21555-25-9; **3,** 21555-26-0; **4,** 21555-27-1; **5,** 21555-28-2; **6,** 21620-44-0; **7,** 15289-81-3; **9,** 71-96-5; **10,** 15289-79-9; **11,** 15289-80-2; **12,** 15456-29-8; **13,** 15456-27-6; **14,** 21555-35-1; **15,** 21555-36-2; diethyl vinyl phosphate, 4851-64-3; 1,1,3,4,4,4-hexachlorobutan-2-one, 21555-45-3; dimethyl 3,4,4-trichloro-1,3-butadien-2-yl phosphate, 21555-46-4.

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