It is seen that in no case does the entrance of hydrocarbon break the kinetic chain.

The over-all chlorophosphonation scheme is summarized in Chart I.

Conclusions

The chlorophosphonation reaction and the oxidation of phosphorous trichloride have been studied in detail. Chlorophosphonation seems to be a competing side reaction in the phosphorous trichloride oxidation. The chlorophosphonation mechanism (Chart I) presented is in essential agreement with that postulated by Mayo.[3]

The kinetic study of the phosphorus trichloride oxidation revealed that this reaction was not spontaneous if sufficient reagent purity was obtained. Apparently the spontaneous nature of the chlorophonation reaction arises from the presence of trace amounts of an initiator (probably hydroperoxides) in the hydrocarbon. Owing to the extreme sensitivity of the phosphorus trichloride oxidation to hydroperoxides, it should be possible to use the rate of phosphorus trichloride oxidation as an analytical method for measuring low concentrations of hydroperoxides.

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Phosphonic Acids and Esters. XV. Preparation and Proton Magnetic Resonance Spectra of the Diethyl α- and β-Chlorovinylphosphonates[1,2]

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The oxidative chlorophosphonation of vinyl chloride has been shown to lead to the formation of dichloroethylphosphonic dichlorides which can be converted by esterification to a mixture of diethyl β,β-dichloroethylphosphonate (**1b**) and diethyl α,β-dichloroethylphosphonate (**2b**). The former ester is the major component of the reaction mixture. In contrast to the results of Soborovskii, it was found that treatment of the mixture of esters with triethylamine leads to rapid dehydrochlorination of **2b** with the formation of diethyl α-chlorovinylphosphonate (**5**); **1b** undergoes a relatively slow dehydrochlorination to yield isomeric *trans*-β-chlorovinylphosphonate (*trans*-**3**). The *trans* ester can also be formed by photolysis of *trans*-1-chloro-2-iodoethylene in the presence of triethyl phosphite; a small amount of *cis*-**3** is also isolated in this reaction. The structures and stereochemistry of the vinylphosphonates (*cis*- and *trans*-**3**, **5**) were established by proton magnetic resonance spectroscopy. Each of these compounds yielded a first-order ABX spectrum and unequivocal assignments of P^{31}–H^1 and H^1–H^1 coupling constants (*gem, cis,* and *trans*) have been made.

As part of an extensive study of the oxidative chlorophosphonation of olefins,[4] Soborovskii, *et al.*,[5] have shown that a mixture of isomeric phosphonic dichlorides results from reactions with unsymmetrical olefins. For example, **1a** (30–35%) and **2** (65–70%) are reported to be formed by the reaction of vinyl chloride, phosphorus trichloride, and oxygen.[5] Since

$$\underset{\textbf{1}}{\mathrm{CHCl_2CH_2P(O)X_2}} \qquad \underset{\textbf{2}}{\mathrm{CH_2ClCHClP(O)X_2}}$$

$$\textbf{a},\ \mathrm{X = Cl};\ \textbf{b},\ \mathrm{X = OC_2H_5}$$

1a and **2a** were inseparable, evidence for their existence was provided by an esterification–dehydrohalogenation sequence. The mixture of esters **1b** and **2b** formed from **1a** and **2a** was also inseparable, but reaction with triethylamine indicated the presence of two materials. The β,β-dichloro ester (**1b**) was reported to undergo dehydrohalogenation to yield diethyl β-chlorovinylphosphonate (**3**) while the α,β isomer (**2b**)

$$\underset{\textbf{3}}{\mathrm{CHCl{=}CHP(O)(OC_2H_5)_2}}$$

was reported to be unreactive. The latter isomer did, however, undergo dehalogenation on reaction with zinc to yield diethyl vinylphosphonate (**4**). The failure of **2b** to undergo dehydrohalogenation with triethylamine was surprising, particularly in view of the later report by Medved and Kabachnik[6] that the reaction of **2a** with ethanol and triethylamine in ether led to the formation of a dehydrohalogenated product, diethyl α-chlorovinylphosphonate (**5**). This observation

$$\underset{\textbf{5}}{\mathrm{CH_2{=}CClP(O)(OC_2H_5)_2}}$$

indicated that **5** should also have been formed in the reaction of the mixture of **1b** and **2b** with triethylamine.

In order to clarify this point and to obtain samples of **3** and **5** for use in Diels–Alder and proton magnetic resonance (pmr) studies, the oxidative chlorophosphonation of vinyl chloride has been reinvestigated. Following the procedure of Soborovskii,[5] equal volumes of vinyl chloride and oxygen were passed through phosphorus trichloride until reaction ceased. Distillation gave a phosphonic dichloride fraction with physical constants comparable with those reported[5] for the mixture of **1a** and **2a**; no separation of the mixture could be achieved by distillation. The pmr spectrum of this provided little structural information. Complex second-order multiplets centered at τ = 3.6, 5.3, 5.7, and 6.1 ppm were observed; elements

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(1) This study was supported in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant No. AF-AFOSR-470-64.

(2) Part XIV: R. H. Churi and C. E. Griffin, *J. Am. Chem. Soc.*, **88**, 1824 (1966).

(3) National Science Foundation Cooperative Graduate Fellow, 1961–1964.

(4) For a summary of these studies, see G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, pp 172, 173.

(5) L. Z. Soborovskii, Y. M. Zinov'ev, and L. I. Muler, *J. Gen. Chem. USSR*, **29**, 3907 (1959).

(6) T. Y. Medved and M. I. Kabachnik, *Izv. Akad. Nauk SSSR., Otdel. Khim. Nauk*, 270 (1961); *Chem. Abstr.*, **55**, 20922 (1961).

of two superimposed AB_2X spectra, consistent with the presence of both **1a** and **2a**, were detected, but an analysis could not be carried out because of extensive multiplet overlap.[7] Attempted gas-liquid partition chromatographic (glpc) analysis of this product was unsuccessful because of extensive reaction with the liquid phase.

The mixture of phosphonic dichlorides was esterified by treatment with absolute ethanol at $-5°$ following the established procedure.[5] Distillation gave a low boiling fraction (12%) which was shown to consist mainly of diethyl vinylphosphonate (**4**) by comparisons of its pmr and infrared spectra with those of an authentic sample. A higher boiling fraction (70%) with physical characteristics similar to those ascribed to the mixture of **1b** and **2b**[5] was also isolated. The gas-liquid chromatogram of this fraction showed a single broad unresolved peak. Absorptions characteristic of diethyl phosphonate functions were observed in the infrared; the presence of a weak absorption at 1629 cm^{-1} indicated the presence of a trace amount of an unsaturated contaminant. The pmr spectrum of this fraction also indicated the presence of **1b** and **2b**, although the multiplicity was such that a complete interpretation could not be obtained. Complex multiplets centered at τ 3.8 and 6.0 and a triplet ($-O-CH_2-CH_3$, $J_{HH} = 7.1$ cps) at τ 8.63 were observed. The complex at τ 6.0 consisted of the typical absorption of a $P-O-CH_2-CH_3$ group superimposed on a more complex methine or methylene absorption.

In an effort to gain further information regarding the composition of this mixture of esters, an authentic sample of the α,β-dichloro ester (**2b**) was prepared by the noncatalyzed addition of chlorine to diethyl vinylphosphonate (**4**). The infrared spectrum of **2b** was compatible with its assigned structure and all of the absorptions of **2b** were observed in the mixture of **1b** and **2b**. The pmr spectrum of **2b** was consistent with the assigned structure; a triplet ($-O-CH_2-CH_3$, $J_{HH} = 7.1$ cps) at τ 8.73 and a complex multiplet (τ 5.50–6.70) were observed. Integrated intensities indicated that the low-field multiplet consisted of the ester methylenes plus the methylene and methine of the $CH_2ClCHCl$ group. Because of signal overlap, the low-field multiplet could not be analyzed. The lack of any absorption for **2b** at fields lower than τ 5.50 allows a more complete interpretation of the spectrum of the mixture of **1b** and **2b**. The multiplet at τ 3.8 in the spectrum of the mixture can be assigned to the methine proton ($CHCl_2$) of **1b**; this multiplet consists of a doublet of triplets as anticipated from coupling with both the phosphorus and the methylene protons.[9] Based upon this assignment and the integrated intensities in the spectrum of the mixture of **1b** and **2b**, the mixture consists of 59% **1b** and 31% **2b**, conclusions counter to those reached by Soborovskii.[5]

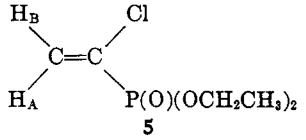
The mixture of esters was then treated with triethylamine in ether following the established procedure;[5] 30% of the theoretical amount of triethylammonium chloride was isolated. Distillation of the reaction mixture gave two fractions in 28 and 50% yield which possessed the physical characteristics reported by Soborovskii[5] for **3** and **2b**, respectively. The infrared spectrum and glpc behavior of the major fraction were essentially identical with those of the starting mixture of esters. A sample of this material was isolated by preparative scale glpc and its pmr spectrum (Table I) indicated it to be essentially uncontaminated **1b**. The spectrum was first order and consistent in all respects with the assigned structure. The isolation and spectrum of **1b** thus confirms the assignments made for the composition of the mixture of **1b** and **2b**; the near quantitative recovery of **1b** from the dehydrochlorination reaction indicates that the rate of dehydrochlorination of **1b** is significantly less than that of **2b**.

TABLE I

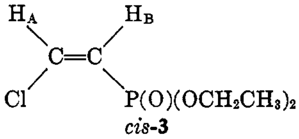
PROTON MAGNETIC RESONANCE PARAMETERS FOR CHLOROETHYL AND CHLOROVINYL PHOSPHONATES[a]

$CH_ACl_2CH_2P(O)(OCH_2CH_3)_2$

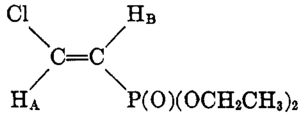
1b



5



cis-**3**



trans-**3**

Compd	Proton	τ	Multiplets	J_{PH}	J_{HH}
1b	A	3.80	Two triplets	8.2	5.4
	B	6.05	Two doublets	6.4	5.4
	$-OCH_2-$	5.78	Two quartets	7.9	7.0
	$-CH_3$	8.73	Triplet	...	7.0
5	A	3.63	Two doublets	13.6	1.1
	B	3.91	Two doublets	35.9	1.1
	$-OCH_2-$	5.90	Two quartets	7.9	7.1
	$-CH_3$	8.62	Triplet	...	7.1
trans-**3**	A	2.92	Two doublets	13.6	14.5
	B	3.96	Two doublets	11.7	14.5
	$-OCH_2-$	5.95	Two quartets	8.1	7.0
	$-CH_3$	8.65	Triplet	...	7.0
cis-**3**	A	3.00	Two doublets	40.3	9.2
	B	3.93	Two doublets	10.7	9.2
	$-OCH_2-$	5.90	Two quartets	8.2	7.2
	$-CH_3$	8.65	Triplet	...	7.2

[a] Spectra were determined in carbon tetrachloride (25–30% by vol). Details are given in the Experimental Section.

Glpc analysis of the minor fraction from the dehydrochlorination reaction indicated it to consist of four materials; this fraction had been identified by Soborovskii[5] as **3**. Preparative-scale glpc led to the isolation of each of these four products and two of the minor products were identified as triethyl phosphate (11.2%) and diethyl chloromethylphosphonate (8.3%) by infrared and pmr comparisons with authentic samples. The two remaining constituents of this

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[7] The presence of a third material in this product was indicated by the nature of the multiplet centered at τ 6.1. This multiplet possessed the structure and symmetry characteristic of the eight inner and most intense lines of an A_2X_2 system;[8] a full analysis could not be carried out since the four outer lines were obscured by other absorptions. The structure (possibly P-CH-CH-P) giving rise to this multiplet is apparently destroyed in subsequent reactions since no multiplet of this type is observed in the spectrum of the esterification products.

[8] H. M. McConnell, A. D. McLean, and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[9] This assignment is substantiated by the spectrum of the sample of **1b** isolated from the dehydrochlorination reaction.

mixture were identified as diethyl *trans*-β-chlorovinylphosphonate (*trans*-**3**, 11.0%) and diethyl α-chlorovinylphosphonate (**5**, 69%). The same results are obtained by treatment of the starting mixture of phosphonic dichlorides (**1a** and **2a**) with triethylamine and ethanol.

These results indicate that, contrary to the conclusions of Soborovskii,[5] the major product of the dehydrohalogenation of the esters **1b** and **2b** is the α-chloro (**5**) rather than the β-chloro (**3**) isomer. Treatment of the mixture of esters with triethylamine leads to a rapid dehydrohalogenation of **2b** with the formation of **5** in accord with the observations of Medved and Kabachnik;[6] under these conditions, the β,β-dichloro ester (**1b**) dehydrohalogenates slowly to yield **3**, the major portion of **1b** being recovered. In order to demonstrate the ease of dehydrohalogenation of **2b**, an authentic sample of the ester was treated with triethylamine under the conditions of the preceding reactions; a quantitative yield of **5** was obtained.

The structures of *trans*-**3** and **5** were assigned on the basis of their pmr spectra (Table I). The vinylic protons of **5** gave a typical ABX spectrum with J_{AB} = 1.1 cps. The value observed for J_{AB} can only be attributed to a geminal proton–proton coupling[10] and is comparable in magnitude to those observed for vinyl chloride (−1.4 cps)[11] and ethyl vinyl ketone (+1.03 cps).[12] The assignment of chemical shifts for the protons *cis* (H_A) and *trans* (H_B) to the phosphonate function were made on the basis of vicinal P^{31}–H^1 coupling constants. The magnitudes of the *trans* (35.9 cps) and *cis* (13.6 cps) P—C=C—H coupling constants reflect the usual stereochemical dependence of vicinal couplings in vinylic systems;[13] the values of these coupling constants are quite similar to those observed in both *trans*- and *cis*-**3** and a number of other vinylphosphonates studied in this laboratory.

trans-**3** also shows an ABX spectrum for the vinylic protons with a vicinal proton–proton coupling constant (J_{AB}) of 14.5 cps. The observed J_{AB} establishes the stereochemistry of this compound since the value is comparable to those observed in a wide range of *trans*-1,2-disubstituted alkenes[10,14–16] (*trans*-β-chloroacrylic acid, 13.2 cps;[14] vinyl chloride, 14.6 cps[15]). The magnitude of the *cis* P—C=C—H coupling (13.6 cps) is the same as that observed in **5**. The geminal P^{31}–H^1 coupling (J_{PB}) is somewhat smaller in magnitude (11.7 cps) than those observed for a number of *trans*-β-substituted vinylphosphonates (15.1–17.9 cps) studied in this laboratory,[17] but comparable to the value found for *cis*-**3**.

Since the over-all yield of *trans*-**3** by the oxidative chlorophosphonation route was quite low, attention was directed to an alternative method of preparation. The most appropriate route appeared to be a modification of the photolytic arylation of trialkyl phosphites.[18] Although the photolysis of vinyl iodides in the presence of trialkyl phosphites had not been examined previously, Kharasch and Gothlich[19] have shown that photolyses of ethynyl and benzoyl iodides provide a satisfactory route to the corresponding radicals. Photolysis of a solution of *trans*-1-chloro-2-iodoethylene[20] in triethyl phosphite led to the isolation of *trans*-**3** in 20% yield. Material of no greater than 95% purity could be obtained by distillation since *trans*-**3** forms an azeotrope with two of the by-products of the reaction, triethyl phosphate and diethyl ethylphosphonate; these impurities were detected and identified by glpc analysis. Pure *trans*-**3** was obtained by preparative-scale glpc and was shown to be identical in all respects with the material isolated from the oxidative chlorophosphonation route. A significant amount of polymeric material was formed during the photolysis reaction. This polymer formation is apparently a result of the photolytic instability of the vinyl iodide since it was shown that *trans*-**3** is unaffected by photolysis.

During the glpc isolation of *trans*-**3**, a small peak (*ca* 2%) with a retention time slightly greater than that of *trans*-**3** was observed. This material was isolated and identified by its pmr spectrum (Table I) as diethyl *cis*-β-chlorovinylphosphonate (*cis*-**3**).[21] As in the cases of **5** and *trans*-**3**, the vinylic absorptions of *cis*-**3** were those of an ABX system with J_{AB} = 9.2 cps. The observed J_{AB} is of the same magnitude as those observed in other *cis*-1,2-disubstituted olefins,[10,14–16] *e.g.*, *cis*-β-chloroacrylic acid, 8.0 cps,[14] vinyl chloride, 7.3 cps.[15] The P^{31}–H^1 coupling constants are consistent with those observed for **5** and *trans*-**3**.

It is interesting to note that for all three chlorovinylphosphonates, the magnitudes of the vicinal P^{31}–H^1 coupling constants parallel the magnitudes of the comparable J_{HH}. The *trans* J_{PH} (36–40 cps) are significantly larger than the *cis* J_{PH} (13.6 cps); the same relationship holds for J_{HH}, although the differences are small (*trans*, 14.5; *cis*, 9.2). The signs of the vicinal H^1–H^1 coupling constants are most probably positive by comparison with values from other systems. No work has been carried out in this system on the determination of P^{31}–H^1 coupling constant signs, but it has been shown that in trivinylphosphine both *cis* and *trans* J_{PH} are positive.[13] It is probable that the cor-

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(10) For a compilation and discussion of geminal and vicinal proton–proton couplings in vinylic systems, see A. A. Bothner-By in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh, Ed., Academic Press Inc. New York, N. Y., 1965, pp 195 ff.

(11) C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 794 (1960); C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 1155 (1962).

(12) S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **37**, 1951 (1962).

(13) The comparable *trans* and *cis* couplings in trivinylphosphine have been shown to be +30.21 and +13.62 cps, respectively [W. A. Anderson, R. Freeman, and C. A. Reilly, *ibid.*, **39**, 1518 (1963)].

(14) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, **30**, 3141 (1965).

(15) N. Muller, *J. Chem. Phys.*, **37**, 2729 (1962).

(16) P. Laszlo and P. R. Schleyer, *Bull. Soc. Chim.* France, 87 (1964).

(17) C. E. Griffin and T. D. Mitchell, *J. Org. Chem.*, **30**, 1935 (1965); M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965; D. C. Wysocki and C. E. Griffin, unpublished results.

(18) J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962); C. E. Griffin, R. B. Davison, and M. Gordon, *Tetrahedron*, **22**, 561 (1966); J. B. Plumb, R. Obrycki, and C. E. Griffin, unpublished results.

(19) N. Kharasch and L. Gothlich, *Angew. Chem.*, **74**, 651 (1962).

(20) The iodoethylene was prepared by the addition of iodine monochloride to acetylene following an established procedure [H. Van de Walle and A. Henne, *Bull. Sci. Acad. Roy. Belg.*, [5] **11**, 360 (1925)]. In our hands, this reaction gave (>95% by glpc and pmr) the *trans* isomer (τ_A 3.34, τ_B 3.52 J_{HH} = 13.4 cps). The dichloroethylenes show J_{HH}: *cis*, 5.2 cps; *trans*, 12.2 cps.[15] This result is at variance with the report of Henne, who obtained a mixture of isomers with a *cis*/*trans* ratio of 5:1. In the present study, no *cis* isomer could be detected.

(21) A sample of this material which had been held at 10° in the dark for six months was found to be significantly altered. Glpc analysis indicated the sample to consist of a mixture of *cis*- and *trans*-**3** and a higher molecular weight product. Further studies of the thermal and photochemical behavior of *cis*- and *trans*-**3** and of the photochemical reaction leading to their formation are in progress and will be reported elsewhere.

responding couplings in the chlorovinylphosphonates are also positive.

Caution. Extreme care must be employed in manipulations of the mixture of dichloroethyl esters and the α-chlorovinyl isomer since, on two occasions, exposure to these materials produced an intense and persistent myosis qualitatively similar to that produced by exposure to diisopropyl phosphorofluoridate.[22] No comparable toxicity was observed for the phosphonic dichlorides (**1a** and **2a**) or the β-chlorovinyl compounds (**3**).

Experimental Section[23]

Formation of Diethyl Chlorovinylphosphonates by Oxidative Phosphonation of Vinyl Chloride.—The procedures employed in the following sequence duplicated the conditions of Soborovskii, *et al.*[5]

Equal volumes of oxygen and vinyl chloride were passed into phosphorus trichloride (600 g) at 20–25° until reaction ceased. Distillation gave a mixture (110 g) of the dichloroethylphosphonic dichlorides (**1a** and **2a**), bp 60–65° (0.2 mm) [lit.[5] bp 74–75° (2.5 mm)]. Attempted glpc analysis of this product on a variety of polar and nonpolar columns was unsuccessful; the product could not be eluted.

The mixture of dichlorides (21.6 g, 0.1 mole) was esterified by dropwise addition to anhydrous ethanol (46.0 g, 1.0 mole) with stirring at −5°. Distillation of the reaction mixture gave two fractions: bp 70–83° (0.2 mm), 2.7 g (12%), and bp 83–93° (0.2 mm), 16.6 g (70%). The higher boiling fraction was shown to be a mixture of the diethyl dichloroethylphosphonates [**1b** and **2b**; lit.[5] bp 108–111° (3 mm)] by pmr and infrared spectra; all of the bands observed in the infrared spectra of pure **1b** and **2b** were observed in the spectrum of the mixture. Extensive decomposition of this mixture was observed during attempted glpc analysis, but the mixture was successfully chromatographed on column A (injection port 150°, column 150°, flow rate 65 ml/min).[24] The mixture was not resolved under these conditions, but was eluted as a single broad peak (retention time 40 min). The lower boiling fraction was shown (pmr and infrared spectra) to be a mixture of **1b** and **2b** and diethyl vinylphosphonate (**4**). The latter compound was isolated by glpc (column B, column 130°, flow rate 80 ml/min, retention time 22 min) and was shown to be identical in all respects with an authentic sample[25] of **4**.

A solution of the mixture of **1b** and **2b** (5.0 g, 0.021 mole) in 20 ml of anhydrous ether was added to a cold (0°) solution of triethylamine (5.0 g, 0.05 mole) in 20 ml of anhydrous ether. When the mixture was allowed to come to room temperature, triethylamine hydrochloride (0.75 g, 26%) precipitated and was removed by filtration. After removal of solvent and amine at reduced pressure, the residue was distilled to yield two fractions: bp 75–81° (1.2 mm) and 85–95° (0.2 mm). The lower boiling fraction (1.0 g) was chromatographed on column B (column 150°, flow rate 80 ml/min.) and shown to consist of four materials. Triethyl phosphate (11.2%, retention time 12 min) and diethyl chloromethylphosphonate (8.1%, retention time 23 min) were isolated and identified by comparisons with authentic samples. Preparative scale chromatography led to the isolation of **diethyl α-chlorovinylphosphonate** (**5**, 69.5%, retention time 16 min) and **diethyl *trans*-β-chlorovinylphosphonate** (*trans*-**3**, 11.2%, retention time 19 min); infrared spectra: **5**, 2994 m, 2941 w, 2915 w, 1600 m, 1481 w, 1445 w, 1389 w, 1370 w, 1262 s, 1166 m, 1117 m, 1088 m, 1023 s, 973 s, 827 m, 798 w, and 741 cm^{-1}; *trans*-**3**, 3067 w, 2994 m, 2941 w, 2911 w, 1583 m, 1485 w, 1449 w, 1394 w, 1372 w, 1255 s, 1187 w, 1167 w, 1100 w, 1025 s, 964 s, 855 w, 833 m, and 738 w cm^{-1}.

Anal. Calcd for $C_6H_{12}ClO_3P$ (**5** and *trans*-**3**): C, 36.25; H, 6.09; P, 15.60. Found (**5**): C, 36.28; H, 5.86; P, 15.50. Found (*trans*-**3**): C, 36.02; H, 6.07; P, 15.67.

The higher boiling fraction (2.5 g) from the original distillation was chromatographed on column A (column 150°, flow rate 65 ml/min) and found to consist of essentially one material with trace amounts of lower boiling constituents. This material was isolated and shown by pmr spectra to be **diethyl β,β-dichlorethylphosphonate** (**1b**); infrared spectrum: 2955 m, 2924 w, 2890 w, 1484 w, 1445 w, 1401 w, 1380 w, 1283 s, 1192 w, 1172 m, 1099 s, 1028 vs, 968 s, 879 w, 779 s, and 724 s cm^{-1}.

Anal. Calcd for $C_6H_{13}Cl_2O_3P$: C, 30.65; H, 5.57; P, 13.18. Found: C, 30.91; H, 5.38; P, 13.47, 13.37.

Preparation of Diethyl α,β-Dichloroethylphosphonate (2b).—Chlorine (9.0 g, 0.25 mole) was added slowly through a bubbler to a solution of diethyl vinylphosphonate (20.0 g, 0.122 mole) in 60 ml of carbon tetrachloride. After the addition was completed, the reaction mixture was refluxed for 1 hr. The solvent was removed under reduced pressure (rotary evaporator) and the residue was distilled to yield 4.0 g of unreacted diethyl vinylphosphonate, bp 45° (0.1 mm), and 5.0 g (17.5%) of **2b**, bp 93–97° (0.1 mm); infrared spectrum: 2994 m, 2941 w, 2911 w, 1484 w, 1452 w, 1402 w, 1381 w, 1320 w, 1272 s, 1160 w, 1093 w, 1018 s, 970 m, 833 w, 790 w, 721 w, and 657 w cm^{-1}.

Anal. Calcd for $C_6H_{13}Cl_2O_3P$: C, 30.65; H, 5.57; P, 13.18. Found: C, 30.80; H, 5.70; P, 13.27.

Higher molecular weight material [8.0 g, bp 125–195° (0.1 mm)] was also isolated during this distillation.

Dehydrohalogenation of Diethyl α,β-Dichloroethylphosphonate (2b).—A solution of 5.0 g (0.021 mole) of **2b** in 20 ml of absolute ether was added at 0° to a solution of 10.0 g (0.10 mole) of triethylamine in 20 ml of absolute ether. When the reaction mixture warmed to room temperature, triethylamine hydrochloride (2.9 g, 98%) precipitated and was removed by filtration. After the solvent was removed under reduced pressure (rotary evaporator), the residue was distilled to give 4.1 g (98%) of **diethyl α-chlorovinylphosphonate** (**5**), bp 49–50° (0.2 mm). This material was identical in all respects with the sample of **5** isolated in the preceding experiment.

Preparation of *trans*-1-Chloro-2-Iodoethylene.—The procedure of Van de Walle and Henne[20] was followed. A stream of acetylene was passed through a solution of 120 g (0.74 mole) of iodine monochloride in hydrochloric acid. Distillation gave 130 g (93%) of *trans*-1-chloro-2-iodoethylene, bp 113–117° [lit.[20] bp 113–114° for *trans*; 116–117° for *cis*]. Pmr and glpc analysis indicated this material to be of >95% purity; infrared spectrum: 3049 m, 1637 w, 1603 w, 1549 w, 1159 s, 1135 w, 911 s, 801 s, and 673 m cm^{-1}.

Photoinitiated Reaction of *trans*-1-Chloro-2-Iodoethylene and Triethyl Phosphite.—A mixture of the iodoethylene (13.0 g, 0.07 mole) and triethyl phosphite (34.0 g, 0.20 mole) was irradiated for 6 hr at 0° in the apparatus previously described. Distillation afforded four fractions: (1) bp 50–68° (15 mm), 27.0 g; (2) bp 45–60° (0.4 mm), 0.5 g; (3) bp 60–67° (0.4 mm), 2.4 g; (4) bp 67–90° (0.4 mm), 0.5 g. Fraction 1 was shown by glpc analysis to consist of triethyl phosphite, triethyl phosphate, diethyl ethylphosphonate, and **diethyl *trans*-β-chlorovinylphosphonate** (*trans*-**3**). Fraction 2 contained *trans*-**3** and triethyl phosphate. Analysis of fraction 3 on column B (column 150°, flow rate 80 ml/min) showed it to consist of *trans*-**3** (85%, retention time 20 min), triethyl phosphate (retention time 12 min), and an unknown material (retention time 46 min). Fraction 4 was shown to consist of *trans*-**3** (50%), a trace of triethyl phosphate, and the unknown. The total yield of *trans*-**3** was 19%; longer or shorter irradiation times did not increase the yield.

The material, bp 60–67° (0.4 mm), from four irradiations was combined and distilled through a 15-in. column packed with glass helices. The fraction, bp 50–53° (0.2 mm), was shown to be 95% *trans*-**3**. Material of analytical purity was obtained by preparative scale glpc on a 20-ft, $^3/_8$-in.-diameter column of 30% silicone rubber SE-30 on Chromosorb P (column 150°, flow rate 250 ml/min, Wilkins Autoprep A-700). *trans*-**3** had a retention

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[22] B. C. Saunders, "Some Aspects of the Chemistry and Toxic Action of Organic Compounds Containing Phosphorus and Fluorine," Cambridge University Press, Cambridge, England, 1957.

[23] Infrared spectra were determined as films on a Beckman IR-8 spectrophotometer calibrated with a polystyrene film. Pmr spectra were obtained on a Varian Associates Model A-60 spectrometer at 37° (probe temperature). Chemical shifts are reported on the τ scale from internal tetramethylsilane (τ = 10.00 ppm); these values are the average of at least two spectral determinations and are accurate to at least ±0.015 ppm. The coupling constants were obtained from 50-cps sweep-width spectra and are the average of at least three runs; the values are accurate to ±0.15 cps or better.

[24] Unless otherwise noted, all glpc analyses were performed on an F & M Model 500 gas chromatograph. The columns employed were A, 6 ft, 20% silicon oil 710 on Chromosorb P; B, 10 ft, 15% Carbowax 20M and 5% Carbowax 1500 on Chromosorb P. Helium was used as carrier gas.

[25] A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947); G. M. Kosolapoff, *J. Am. Chem. Soc.*, **70**, 1971 (1948).

time of 15 min, gave an acceptable elemental analysis, and was identical in all respects with the material isolated previously. A small peak (*ca.* 2%) with retention time of 17 min was also isolated and shown by pmr spectra to be **diethyl *cis*-β-chlorovinylphosphonate** (*cis*-**3**); infrared spectrum: 2998 m, 2950 w, 2915 w, 1585 m, 1484 w, 1449 w, 1398 w, 1374 w, 1323 w, 1263 s, 1173 m, 1105 m, 1030 s, 970 s, 864 w, 829 w, 790 w, and 749 w cm^{-1}.

Anal. Calcd for $C_6H_{13}ClO_3P$: C, 36.25; H, 6.09; P, 15.60. Found: C, 36.51, 36.44; H, 6.19, 6.21; P, 15.88.

A Cyclic Peroxy Ester, β-Methyl-β-phenyl-β-peroxypropiolactone[1]

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The synthesis, properties, and thermal decomposition of the novel peroxygen compound, β-methyl-β-phenyl-β-peroxypropiolactone, are described. The peroxylactone may be prepared by acid-catalyzed reaction of hydrogen peroxide and the hydroxy acid. Decomposition in carbon tetrachloride at 134° affords propiophenone (70%), benzyl methyl ketone (15%), acetophenone (5%), and α-phenylpropionaldehyde (1.5%). Two possibles species, α-methylstyrene oxide and α-methoxystyrene, have been excluded as products or as precursors of the major products; the oxide, however, may be the precursor of the 1.5% of aldehyde observed. Decomposition is first order in peroxylactone and is insensitive to oxygen or azobisisobutyronitrile (ΔH^*, 31.5 kcal/mole; ΔS^*, −0.3 cal/mole per degree). Possible modes of decomposition of the peroxylactone are discussed.

A number of points of interest are associated with the incorporation of the oxygen–oxygen bond in a cyclic system. Such systems may serve as precursors of a variety of biradicals. Secondly, the constraint such systems place on the oxygen–oxygen bond may lead to marked changes in chemical behavior in comparison with acyclic analogs (*e.g.*, phthaloyl peroxide).[3] It was thus of interest to us to examine the chemical consequences of incorporation of the oxygen–oxygen bond in a cyclic perester. This paper reports the synthesis and study of the thermal decomposition of the first example of this class, β-methyl-β-phenyl-β-peroxypropiolactone (**1**).

Results

The peroxylactone, **1**, was prepared by reaction of hydrogen peroxide with β-hydroxy-β-phenylbutyric acid in ether, catalyzed by concentrated sulfuric acid. The structure proof of the peroxylactone, obtained as a low melting solid, is based on spectral and analytical data summarized in the Experimental Section. The carbonyl band in the infrared is at 1810 *vs.* 1750 cm^{-1} for acyclic per esters, a difference somewhat greater than that observed between esters and γ-lactones. The peroxylactone may be titrated by iodometric analysis, does not appear to be shock sensitive, and has thermal stability comparable with that of *t*-butyl peracetate.[4]

Thermal Decomposition.—Decomposition of the peroxylactone in carbon tetrachloride (degassed, sealed tubes) afforded four products, propiophenone, benzyl methyl ketone, acetophenone, and α-phenylpropionaldehyde, analyzed by vpc and identified by collection and comparison with authentic samples. Product studies were made at two temperatures and at two initial concentrations. At 134°, the four principal products account for 93–95% of the peroxylactone.

Table I

Products of the Thermal Decomposition of β-Methyl-β-phenyl-β-peroxypropiolactone in Carbon Tetrachloride

Products	Yield, %		
	107°[a,b]	134°[a,b]	134°[b,c]
$C_6H_5COCH_3$	8.0, 7.9	5.7, 5.6	5.1, 5.1
$C_6H_5CH(CH_3)CHO$	<0.5, <0.5	1.5, 1.5	1.5, 1.5
$C_6H_5CH_2COCH_3$	9.7, 10.8	15.2, 14.9	15.8, 15.7
$C_6H_5COCH_2CH_3$	63.6, 63.0	71.2, 70.0	72.1, 70.7

[a] Initial peroxylactone, 0.0546 *M*; pyridine, 0.1 *M*. [b] Two separate runs. [c] Initial peroxylactone, 0.0254 *M*; pyridine, 0.1 *M*.

Kinetics.—A series of experiments was made to ascertain the principal mode of decomposition of the peroxylactone. The rate of decomposition in carbon tetrachloride alone was close to first order. Excellent first-order behavior was observed upon the inclusion of pyridine, which consequently was also employed in the product studies described above. The rate of disappearance of peroxylactone was unaffected by glass wool, oxygen, or azobisisobutyronitrile (present in severalfold excess over the peroxylactone) indicating the unimportance of surface catalysis or induced decomposition under the conditions of this study. Only a slight increase in rate was observed upon decomposition of peroxylactone in the presence of 0.01 *M* trifluoroacetic acid.

The rate of decomposition was measured over a ninefold variation in initial concentration of peroxylactone and at three temperatures. The results are summarized in Table II.

Table II

Decomposition of β-Methyl-β-phenyl-β-peroxypropiolactone in Carbon Tetrachloride

Temp, °C	Peroxylactone, $M \times 10^2$	$k_1 \times 10^5$ sec^{-1}
126	1.10	4.59 ± 0.05
126	4.86	5.19 ± 0.04
126	9.75	5.15 ± 0.13
134	1.06[a]	9.71 ± 0.08
134	1.03[a]	9.54 ± 0.09
106.8	1.02[a]	0.565 ± 0.005

[a] Pyridine, 0.02 *M*.

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[3] F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **80**, 3432 (1958); **82**, 893 (1960).

[4] See Table I in P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).