SYNTHESIS OF CYCLIC PHOSPHOROUS ACID ESTERS BY TRANSESTERIFICATION¹

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ABSTRACT

Five- and six-membered cyclic phosphorous acid esters were synthesized by transesterification of phosphites with 1,2- and 1,3-glycols: Diethyl hydrogen phosphite was transesterified to give cyclic hydrogen phosphites. Partial transesterification of tris-2-chloroethyl phosphite resulted in cyclic 2-chloroethyl phosphites.

Organic phosphites are potentially important chemicals as antioxidants in the petroleum and plastics industry (1, 2, 3). Their usefulness is limited, however, by their hydrolytic instability. Recently, the extreme resistance of *cis*-1,3-cyclohexylidene phosphate to hydrolysis was reported (4). This report together with earlier knowledge (5) regarding the stability of 2,3-dimethyl-2,3-butylene hydrogen phosphite initiated the present work of synthesizing new cyclic phosphites.

SYNTHESIS OF CYCLIC HYDROGEN PHOSPHITES

One of the earliest methods for synthesizing dialkyl esters of phosphorous acid is the direct esterification (6, 7) by heating phosphorous acid with the appropriate alcohol. The first syntheses of cyclic hydrogen phosphites were probably accomplished by starting from phosphorous acid and various glycols. However, there is little evidence of a single pure product being isolated (8).

Another method for the synthesis of cyclic hydrogen phosphites is the hydrolysis of cyclic chlorophosphites (5, 9, 10, 11) or alkyl phosphites (5). Saunders and his co-workers (12) reported the synthesis of a cyclic secondary diphosphite by reacting phosphorus trichloride with an excess of ethylene glycol.

In the course of this work, the transesterification of diethyl hydrogen phosphite with 1,2- and 1,3-glycols was accomplished. When 3-chloro-1,2-propylene glycol was used for transesterification, the known 3-chloro-1,2-propylene hydrogen phosphite or 2-hydroxy-4-chloromethyl-1,3,2-dioxaphospholane (13) was obtained. Analogously, the formation of other cyclic hydrogen phosphites with five-membered (dioxaphospholane) and six-membered (dioxaphosphorinane) ring structures was presumed according to the following equations:



In the transesterification experiments, 1 mole of 1,2- or 1,3-glycol was used per mole of hydrogen phosphite. The reactions were carried out between 130 and 140° C at

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120–150 mm. When the liberation of the by-proudct ethanol ceased, the remaining crude product was fractionated at pressures between 2 and 3 mm. The purified compounds are liquids with the exception of the white crystalline 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinane. Some of the physical and analytical data and the yields of the compounds obtained are shown in Table I.

TABLE I	
Cyclic hydrogen phosp	hites

		Refractive	Phosphorus (%)		37.11
Formula	B.p. (° C/mm)	$(n_{\rm D}^{20})$	Calc.	Found	(%)
CH ₃ -CH-O L CH-O CH-O O CH-O	84-86/2.3	1.4580	25.4	23.9	78
CH ₂ —O CH ₂ —O CH ₂ —O O	97-98/2.5	1.4522	25.4	24.9	79
CH ₃ −CH−O CH ₃ −CH−O CH ₃ −CH−O O	84-85/2.3	1.4616	22.8	23.1	75
CH ₃ -CH-O HC ₂ P-H CH ₂ -O O	103-104/2.3	1.4547	22.8	22.8	76
$CH_2 = O$ $C_2H_3 = CH$ $P = H$ $C_3H_7 = CH = O$	117-118/2.5	1.4600	16.1	16.3	78
$(CH_3)_2C$ $P-H$	103-104/2.3	nı.p. 53–55°	20.6	20.2	85
$CICH_2 - CH - O $ $\downarrow P - H^*$ $CH_2 - O $	125126/2.3	1.4910	19.8	19.7	83
$H \xrightarrow{P} O \xrightarrow{O - CH_2CH_2 - O} P \xrightarrow{P - H} O \xrightarrow{O - CH_2CH_2 - O} O \xrightarrow{P - H} O$	117-118/2.3	1.4751	28.7	28.2	56

*First synthesized by Arbuzov and Zoroastrova (10).

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n an airte an an tha tha an an airte Chlumh a' fhailte an ann an tha fhail Unequivocal syntheses of the cyclic butylene hydrogen phosphites were also carried out to prove the five- and six-membered ring structures respectively. These syntheses started from the appropriate butanediols and phosphorus trichloride. In this manner, the corresponding cyclic chlorophosphites (11, 12) were prepared. These compounds yielded the cyclic hydrogen phosphites after hydrolysis with the stoichiometric amounts of water. CANADIAN JOURNAL OF CHEMISTRY. VOL. 37, 1959



It can be assumed from the high yield of the product of hydrolysis that the water attack results in the selective removal of the chlorine without ring opening. The identity of the infrared spectra of the compounds obtained in this manner with the butanediol transesterification products verifies the assumed five- and six-membered ring structures.

All the liquid cyclic hydrogen phosphites prepared are highly viscous materials with high boiling points. These properties probably indicate intermolecular association as shown by B. A. Arbuzov and Vinogradova (13) in the case of dialkyl phosphites. In the case of the hydrogen phosphite tautomer such an association can be depicted as follows:



This assumption is supported by the observation that the cyclic hydrogen phosphites prepared from the chlorophosphites became viscous only after several days' standing after distillation.

Transesterification with ethylene glycol resulted in a compound having an identical boiling point with the cyclic diethylene diphosphite mentioned previously.

SYNTHESIS OF CYCLIC PHOSPHITES

Transesterification of phosphite esters was first performed by Milobendzki and Szulgin (14). They prepared propyl- and butyl-diphenyl phosphite from triphenyl phosphite by the action of the corresponding sodium alcoholates according to the following equation:

$$(Ph-O)_{3}P + NaOR \rightarrow (Ph-O)_{2}POR + Ph-ONa.$$

Some patents claim transesterification of triarylphosphites with alcohols (1, 2); for example, the synthesis of alkyl diaryl phosphites by the following reaction:

$$(ArO)_{3}P + HOR \rightarrow (ArO)_{2}POR + HOAr.$$

A recent German patent (15) claims the transesterification of tris-2-chloroethyl phosphite with several alcohols. However, in this work the transesterification reaction with polyhydric alcohols was mentioned as giving polymeric products.

The reinvestigation of the latter transesterification in these laboratories revealed some new facts suggesting the formation of monomeric cyclic phosphite esters by partial transesterification of tris-2-chloroethyl phosphite with 1,2- and 1,3-glycols.

In previous work, cyclic phosphite esters have also been synthesized from the corresponding cyclic chlorophosphites, which in turn were prepared from phosphorus trichloride and diols; in both cases with the help of an acid-binding agent (pyridine) (10, 11, 16, 17).

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$$(R_{2}C)_{n}(OH)_{2} + PCl_{3} + 2C_{5}H_{5}N \rightarrow (R_{2}C)_{n} \bigcirc PCl + 2C_{5}H_{5}N . HCl$$

$$(R_{2}C)_{n} \bigcirc P-Cl + HOR + C_{5}H_{5}N \rightarrow (R_{2}C)_{n} \bigcirc P-OR + C_{5}H_{5}N . HCl$$

Similar compounds can be synthesized starting with an alkyl dichlorophosphite and a diol.

$$\operatorname{ROPCl}_{2} + (\operatorname{HO})_{2}(\operatorname{CR}_{2})_{n} + 2\operatorname{C}_{5}\operatorname{H}_{5}\operatorname{N} \to \operatorname{ROP} \bigvee_{O}^{O} (\operatorname{CR}_{2})_{n} + 2\operatorname{C}_{5}\operatorname{H}_{5}\operatorname{N} \cdot \operatorname{HCl}$$

Cyclic catechol phosphites were prepared by an analogous method starting from catechol and phosphorus trichloride (18, 19). Chloroethyl catechol phosphite was synthesized by reacting ethylene oxide with catechol chlorophosphite according to the following reaction equation (20):

$$\begin{array}{c} & O \\ & O \\ & O \end{array} P - Cl + CH_2 - CH_2 \rightarrow O \\ & O \\ & O \end{array} P - OCH_2CH_2Cl.$$

The stability of the cyclic phosphite esters is greatest for six-membered rings (10, 11, 16, 17).

Partial transesterification of 1 mole of tris-2-chloroethyl phosphite with 1 mole of 1,2- or 1,3-glycol was attempted. At elevated temperature and reduced pressure about 2 moles ethylene chlorohydrin per mole of phosphite was removed from the reaction mixture as indicated by the amount of the distillate in the receiver and the weight loss of the reaction mixture. After redistillation, the distillate was identified as ethylene chlorohydrin by boiling point, refractive index, and infrared spectrum. The formation of five- and six-membered cyclic chloroethyl phosphites is suggested according to the following general equations:

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The lower glycols used in these reactions were not miscible with the tris-2-chloroethyl phosphite, but after standing at room temperature homogeneous mixtures were obtained. For preparative purposes, the reaction was performed by heating the ingredients between 60 and 100° C *in vacuo*, and the ethylene chlorohydrin distilled as it was formed. The remaining crude product was fractionated *in vacuo* yielding the purified, colorless cyclic chloroethyl phosphites usually as liquids, immiscible with water. Some of the physical and analytical data and the yields obtained are shown in Table II.

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TABLE II Cyclic 2-chloroethyl phosphites								
	B.p. (° C/mm)	Refractive index – (n ²⁰ _D)	Chlorine					
Formula			Calc.	Found	- Yield (%)			
CH_{3} CH_{3} CH_{2} CH_{2} $CH_{2}CH_{$	105-107/2	1.4534	15.67	16.05	80			
$CH_{3}-CH-O$ CH_{2} $P-OCH_{2}CH_{2}CI^{*}$ $CH_{2}-O$	98–100/2.3	5 1.4680	17.88	18.30	75			
CH ₃ CHO CH ₃ CHO POCH ₂ CH ₂ Cl*	107-109/3	1.4650	17.88	17.90	70			
$CICH_{2}CH_{2}O - P \begin{pmatrix} O - CH_{2}CH_{2} - O \\ O - CH_{2}CH_{2} - O \end{pmatrix} P - OCH_{2}CH_{2}CI^{\dagger}$	108-110/2	1.4898	20.82	19.85	20‡			
P-OCH ₂ CH ₂ Cl§	82 - 84/2	1.5390	16.24	16.50	85			

*For data on compound prepared by independent synthesis see Experimental part.

†Highly viscous liquid; tentative formula. For ethylene-2-chloroethyl phosphite Arbuzov (10) gives the following data: b.p. 78.5–79.5° at 65 mm, n_D^{\odot} 1.4755.

‡The greater part of the raw product is polymeric material, which cannot be distilled.

§Previously prepared by Kabachnik (20), who found b.p. $107-108^{\circ}$ at 2.5 mm and n_D^{20} 1.5430. Catechol-2-chloroethane-phosphonic acid has b.p. $167-170^{\circ}$ at 4.5 mm and n_D^{20} 1.5502 as reported by Kabachnik and co-workers (21).

Unequivocal syntheses of the cyclic butylene 2-chloroethyl phosphites were also carried out to prove the five-membered 1,3,2-dioxaphospholane and the six-membered 1,3,2-dioxaphosphorinane ring structures respectively. In these syntheses the corresponding cyclic chlorophosphites (10, 11) were reacted with ethylene chlorohydrin to give the cyclic 2-chloroethyl phosphites.

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}-\mathrm{O}\\ \mathrm{CH}_{3}-\mathrm{CH}-\mathrm{O}\\ \mathrm{CH}_{3}-\mathrm{CH}-\mathrm{O}\\ \mathrm{CH}_{2}-\mathrm{CH}-\mathrm{O}\\ \mathrm{CH}_{2}-\mathrm{O}\\ \mathrm{CH}$$

In the course of these reactions, if carried out below room temperature, Arbuzov transformation and ring opening are not likely to occur. Therefore, the identity of the infrared spectra of the compounds with the corresponding transesterification products supports the presence of the cyclic phosphite structures. A further indication of this structure is given by the comparison of the boiling point and refractive index of the catechol transesterification product with catechol 2-chloroethyl phosphite prepared by Kabachnik (20) from catechol chlorophosphite.

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EXPERIMENTAL

Preparation of Cyclic Hydrogen Phosphites by Transesterification

Diethyl hydrogen phosphite (27.6 g, 0.2 m (mole)) and 1,2- or 1,3-glycol (0.2 m) were placed in a round bottom flask connected to a Claisen head fitted with a downward condenser and a receiver for vacuum distillation. The resulting solution was heated to 130° C at 120-160 mm pressure under nitrogen. The reaction proceeded as shown by the distillation of ethanol. Ethanol evolution ceased after about 3 hours' heating at the above temperature.

The remaining crude product was fractionated at 2 to 3 mm. The cyclic hydrogen phosphites were obtained as very viscous, colorless liquids. The yields and other data are given in Table I. Some high boiling materials remained in the distillation flask and were probably polymeric.

Preparation of Cyclic Chlorophosphites

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To a solution of phosphorus trichloride (68.7 g, 0.5 m) in anhydrous ether (200 ml) a mixture of 2,3- or 1,3-butanediol (45 g, 0.5 m), pyridine (79 g, 1 m), and ether (200 ml) was added with vigorous stirring, while the temperature was kept below -5° C. The precipitated pyridinium chloride was removed by filtration and washed with ether. The combined clear filtrate was fractionated. After the removal of the ether, the cyclic chlorophosphites were distilled in vacuum and were obtained as colorless liquids.

Starting from 2,3-butanediol, 67 g (87%) 2-chloro-1,3,2-dioxaphospholane boiling at 54-56° C at 10 mm was obtained. The refractive index was $n_{\rm D}^{20}$ 1.4700. (Lucas and coworkers (11) obtained apparently the same product without an acid-binding agent. It had a boiling point of 66° C at 15 mm and a refractive index of $n_{\rm D}^{20}$ 1.4696.)

When 1,3-butanediol was used, the method gave 2-chloro-4-methyl-1,3,2-dioxaphosphorinane (69.5 g, 98%) boiling at 55–57° C at 10 mm. The refractive index of this product was $n_{\rm D}^{20}$ 1.4670. (Arbuzov and Zoroastrova (10) reported b.p. 65° C at 12 mm and $n_{\rm D}^{20}$ 1.4700. Lucas and co-workers (11) gave b.p. 66.6–67.5° C at 15 mm and $n_{\rm D}^{20}$ 1.4884.)

Synthesis of Cyclic Hydrogen Phosphites by the Hydrolysis of Cyclic Chlorophosphites

To a mixture of water (3.6 g, 0.2 m) and benzene (100 ml), the solution of the chlorophosphite (0.2 m) in benzene (250 ml) was added, while it was shaken. The reaction mixture was then stirred for one-half hour. The resultant clear, homogeneous solution was fractionated in vacuum, when the benzene solvent was removed at first under 160 mm pressure. The raw product was then distilled at 2 mm of mercury.

2-Chloro-4,5-dimethyl-1,3,2-phospholane gave on hydrolysis 2-hydroxy-4,5-dimethyl-1,3,2-phospholane (26 g, 95%). The product was obtained between 81° and 83° C at 2 mm and had a refractive index, $n_{\rm D}^{20}$ 1.4610. Comparison of infrared spectra showed identity with the 2,3-butanediol transesterification product.

Similarly, by the hydrolysis of 2-chloro-4-methyl-1,3,2-phosphorinane, this procedure resulted in the formation of 2-hydroxy-4-methyl-1,3,2-dioxaphosphorinane obtained as a colorless liquid (25 g, 92%) between 101 and 102° C at 2 mm. The refractive index is $n_{\rm D}^{20}$ 1.4528. Although this product was a mobile liquid after distillation, it became quite viscous after a few days and was similar to the transesterification product with 1,3-butanediol. The identity of the two products was then proved by comparison of their infrared spectra.

Preparation of Cyclic 2-Chloroethyl Phosphites by Transesterification

Tris-2-chloroethyl phosphite (26.9 g, 0.1 m) and 1,2- or 1,3-glycol (0.1 m) were placed in a round bottom flask connected with a Claisen head, downward condenser, and receiver

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for vacuum distillation. The contents became homogeneous within 5 minutes when heated in a water bath. Reaction was performed at 18 mm under nitrogen. The heating was continued for about 1 hour, during which time the evolution of ethylene chlorohydrin was complete.

The colorless crude product was fractionated at 2-3 mm pressure to obtain the pure products as clear, colorless liquids, immiscible in water. See Table II for properties and yields.

Preparation of Cyclic 2-Chloroethyl Phosphites from Cyclic Chlorophosphites

To a solution of the cyclic chlorophosphite (30.9 g, 0.2 m) (2-chloro-4,5-dimethyl-1,3,2dioxaphospholane and 2-chloro-4-methyl-1,3,2-dioxaphosphorinane respectively) in ether (200 ml), ethylene chlorohydrin (16.1 g, 0.2 m) and subsequently pyridine (15.8 g, 0.2 m) were added dropwise with stirring at 0° C or lower. After the addition, the reaction mixture was allowed to come to room temperature with continued stirring. Pyridinium chloride was removed by filtration and the filtrate was fractionated.

In this manner, beginning with 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane between 56 and 60° C at 1 mm, 31 g (79%) 2-(β -chloroethoxy)-4,5-dimethyl-1,3,2-dioxaphospholane (2,3-butylene-2-chloroethyl phosphite) was obtained, $n_{\rm p}^{20}$ 1.4659. The spectrum of this compound was identical with the product of transesterification reported in Table II.

When the same method was used, 2-chloro-4-methyl-1,3,2-phosphorinane gave 33 g (86%) 2-(β -chloroethoxy)-4-methyl-1,3,2-dioxaphosphorinane distilled between 54 and 56° C at 1 mm and having a refractive index of $n_{\rm D}^{20}$ 1.4697. This compound had an identical spectrum with the corresponding transesterification product reported in Table II.

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