Reactions of P(III) Chlorides with Aldehydes: I. Synthesis of Primary Intermediates of the Reactions of Aliphatic Aldehydes with P(III) Chlorides Possessing Electrophilic Properties

M. B. Gazizov, R. A. Khairullin, and R. F. Karimova

Kazan National Research Technological University, ul. K. Marksa 68, Kazan, Tatarstan, 420015 Russia e-mail: mukattisg@mail.ru

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Abstract—An approach to investigation of reactions of electrophilic P(III) chlorides with aliphatic aldehydes is developed. Its essence is the removal of HCl impurity from chloride and catalytic blocking of electrophilic center of the carbonyl group. For these purposes nitrogen-containing organic bases and alkyl vinyl ethers are used. Three types of primary intermediates with the nearest P(III) environment POCl₂, O_2PCl , and O_3P are synthesized. It is established that the stability of intermediates increases with the growing acceptor properties of substituents at P(III) and donor properties of the aldehyde fragment.

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One of the reactions used in organophosphorus chemistry for the synthesis of substances with C-P(IV) bond is the interaction of P(III) chlorides I with aldehydes II described for the first time in [1]. It was established that phosphorus trichloride Ia vigorously reacted with aldehydes II to give viscous oils. These addition products due to the ambiguity of their structure were called adducts.

$$\begin{array}{c} PCl_3 + RCHO \rightleftharpoons [Adduct].\\ Ia II \end{array}$$

If the adduct is subjected to pyrolysis it gives stable 1-chloroalkyl derivatives III [2–3]. Its hydrolysis under mild conditions leads to 1-hydroxyalkanephosphonic acids IV [4–8].



In contrast to [9, 10] the studies [2-5] showed that P(III) chloride is an electrophile, and the coordination of phosphorus atom in the primary process is retained. Therefore the reaction products are 1-chloroalkyl P(III) derivatives **V**.

In the case of phosphorus trichloride **Ia** the gradual substitution of chlorine atom with 1-chloroalkoxyl group and the formation of mono- **VI**, di- **VII**, and tri-(1-chloroalkyl)phosphites **VIII** was suggested. These substances undergo isomerization to P(IV) derivatives **IX** [2].

Taking into account the influence of the nature of substituents at P(III) in compounds I on the readiness of the reaction proceeding it was concluded that PCI_3 and P(III) dichlorides exhibited the electrophilic [11–17] and monochlorophosphines the nucleophilic reactivity [14, 18–20].

The reactivity of phosphoromonochloridites depends on the nature of hydrocarbon substituents bound with the oxygen atom. If this moiety is phenyl (as in diphenyl chlorophosphite) or 1,2-phenylene (as in catechol chlorophosphite) P(III) monochloride exhibits electrophilic reactivity [21]. If it is an unsubstituted alkyl group, phosphoromonochloridites on different stages of the reaction exhibit nucleophilic as well as electrophylic reactivity and form polymeric products [22].

Proceeding from the structure of P(IV) 1-chloroand 1-hydroxyderivatives III, IV it was suggested that in the course of the formation of adduct one molecule of aldehyde was consumed per each P–Cl bond. But since the middle of nineteen seventies a series investigations has shown that two molecules of aldehyde are consumed per one P–Cl bond [11–14, 17–19, 21]. It has been shown [13, 17, 21] that in the reactions of PCl₃, ethyl- and phenyldichlorophosphines with aliphatic aldehydes compound XI is the main component of adduct. They are formed evidently as a result of isomerization of intermediate substances with $P(III) \mathbf{X}$.

$$\begin{array}{c} X(\text{RCHClOCHRO})\text{POCHROCHRCl}\\ X\\ \rightarrow X(\text{RCHClOCHRO})\text{P(O)CHROCHRCl}\\ XI \end{array}$$

$$X = Et, Ph, Cl, RCHClOCHRO.$$

But compounds **XI** contain labile P(O)OCHRO· CHRCl fragment. By treating with PCl_5 they were converted to stable P(IV) chlorides **XII** which were isolated in the pure state: Et(Cl)P(O)CHROCHRCl **XIIa**, Ph(Cl)P(O)CHROCHRCl **XIIb**, and Cl₂P(O)· CHROCHRCl **XIIc**.

Summarizing the above data on the reactions of P(III) chlorides having electrophilic properties with aliphatic aldehydes under mild conditions (25–80°C) the following general scheme can be suggested.

$$R^{1}R^{2}PCI + R^{3}CHO \implies R^{1}R^{2}POCHR^{3}CI^{-} \implies R^{1}R^{2}POCHCIR^{3}$$

$$XIII \qquad XIV$$

$$\stackrel{+RCHO}{\longrightarrow} R^{1}R^{2}POCHR^{3}OCHR^{3}CI^{-} \implies R^{1}R^{2}POCHR^{3}OCHCIR^{3} \implies R^{1}R^{2}P(O)CHR^{3}OCHCIR^{3}$$

$$XV \qquad X \qquad XI$$

The nucleophilic attack of the carbonyl group oxygen on the electrophilic P(III) atom leads to the ion pair **XIII** which converts to the addition product of P(III) chloride to one molecule of aldehyde or in a product of substitution of a chlorine atom on P(III) by 1-chloroalkoxy group **XIV**. The structure **XIV** is the first intermediate of this reaction. It adds the next aldehyde molecule to give new ion pair **XV** with two fragments of aldehyde and then converts to compound **X** containing 1-(1-chloroalkoxy)alkoxy group at P(III). The product **X** is the second intermediate of the reaction. When the nucleophilicity of P(III) is sufficient it undergoes isomerization to P(IV) derivative **XI**.

Though the structure of primary intermediates **XIV** is considered to be universally adopted, they were neither isolated nor detected by spectral methods. It was assumed that the second aldehyde molecule in the presence of acidic admixtures adds very rapidly and intermediates **XIV** hardly could be isolated. It was therefore necessary to work up a quite new approach to the investigation of these reactions with the purpose of separating the stages of addition of the first and the second aldehyde molecules to one P–Cl bond.

It must be emphasized here that catalytic effect of HCl impurity in P(III) chlorides was found in the reactions with many O-containing organic substances like alkene oxides [23], carboxylic acids [24], acetals [25], and aldehydes [20]. It proved that P(III) chloride purified from HCl admixture by treating with alkyl vinyl ethers did not react with aldehydes and acetals at 20°C. The reaction begins only by bringing HCl in the reaction mixture by various ways [20]. Hence, the problem of separation the stages of addition of the first and the second aldehyde molecules to one P–Cl bond can not be solved only by removing acidic admixtures from P(III) chlorides.

We also knew that P(III) chlorides, in particular, catechol chlorophosphite **Ib**, reacted with aldehydes activated by such nucleophiles as trialkyl phosphites **XVI** and triethylamine **XVIIa** expending one molecule of compound **II** per each P–Cl bond.

New C–X (X = P [26, 27], N [28, 29]) is formed, and the coordination number of phosphorus atom originally bound with chlorine does not change leading to compounds **XVIII**, **XIX**.



We suggested that nucleophiles **XVI**, **XVIIa** not only activate the calbonyl group, but also protect the electrophilic center from the addition of the second aldehyde molecule.

We have found [29, 30] that the reaction with triethylamine is reversible. Under mild conditions $(-10^{\circ}C)$ the salt **XIX** is comparatively stable and

precipitates during the reaction progress. At 20°C its decomposition becomes noticeable especially under continuous removing of the products of decomposition from the reaction medium. If the salt **XIX** contacts with excess triethyl phosphite for 30 days, compound **XX** containing two phosphorus atoms is formed according to the Birum reaction.



Salt XIX was reported [28] to be transformed at heating in a vacuum to vinylpyrocatechol phosphite, but the temperature of the transformation was not mentioned. We have found that while heating at 110– 120°C in a vacuum salt XIX completely decomposes into starting substances, and initial chloride **Ib** is formed in a good yield. Considering the reversibility of the reaction in the case of amine **XVIIa** we suggested that using it in a relatively low concentrations would permit the synthesis of the primary intermediates **XIV**. Due to that the essence of the approach we developed was the removal of acidic impurities from the P(III) chloride and the catalytic blocking of the electrophilic center of the carbonyl group. Preliminary results we reported recently [30–32]. This goal was achieved by using compounds possessing basic and nucleophilic properties like tertiary amines **XVII** and alkyl vinyl ethers **XXI**.

We have developed three methods of synthesis of primary intermediates using tertiary amines (method a), alkyl vinyl ethers (method b), and transformation of one primary intermediate into another (method c).

While treating P(III) chloride with tertiary amine HCl admixture transforms in amine hydrochloride **XXII**. Usually compounds **I** and **XVII** are mixed at room temperature in 1.0 : 0.10–0.15 ratio and P(III) chloride is distilled directly into the reaction flask [31]. Amine hydrochloride **XXII** remains in the still.

$$PCI \cdot HCI + \ddot{B} \longrightarrow PCI + B \cdot HCI$$

$$XVII \qquad XXII$$

$$PCI \cdot HCI + CH_2 = CHOR \longrightarrow PCI + CH_3CH(OR)CI$$

$$XXI \qquad XXIII$$

According to another procedure P(III) chloride and alkyl vinyl ether are mixed in 1.0 : 1.0 ratio at 10° C. α -Chloroether **XXIII** obtained and excess alkyl vinyl ether are removed in a vacuum, and compound **I** is

distilled into the reaction flask [30]. It turned out that alkyl vinyl ethers are convenient for purification of high boiling P(III) chlorides, but they are unsuitable for purification of PCl_3 . The latter vigorously reacts

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with alkyl vinyl ethers to give organophosphorus compounds with P–C bond [33] and also promotes their polymerization. Tertiary amines have appeared to be more universal. They can be used for purification of practically all P(III) chlorides including PCl₃. Regardless of the boiling point of P(III) chloride low boiling trialkylamines and high boiling organic bases like *N*,*N*-dialkylanilines can be used.

We have synthesized primary intermediates which by the character of nearest P(III) environment (OPCl₂, O_2PCl , and O_3P) were divided in three types. P(III) atoms with the analogous environment are present in previously mentioned compounds **VI**, **VII**, and **VIII**. Their numbers are retained by us as general for three types of intermediates.

$\begin{array}{c|cccc} RCHClOPCl_2 & R^1CHClOP(OR^2)Cl & R^1CHClOP(OR^2)(OR^3) \\ \hline VI & VII & VIII \end{array}$

VII, $R^1 = Me$, $R^2 = MeCHCl$ (**a**), $R^1 = i$ -Pr, $R^2 = CCl_3CH_2$ (**b**); **VI**, R = Me (**a**), p-Pr (**b**), i-Pr (**c**), CCl_3 (**d**); **VII**, **VIII**, $R^1 = Me$, $R^2 = R^3 = MeCHCl$ (**a**), $R^1 = i$ -Pr, $R^2 = R^3 =$ CCl_3CH_2 (**b**), Ph (**c**), $R^1 = i$ -Pr, $R^2 = CCl_3CH_2$, $R^3 =$ i-PrCHCl (**d**), $R^1 = Me$, $R^2 = CCl_3CH_2$, $R^3 = MeCHCl$ (**e**), $R^1 = i$ -Pr, $R^2 = R^3 = Me$ (**j**), Et (**k**), $R^2 = R^3 = 1,2$ -C₆H₄, $R^1 =$ Me (**g**), i-Pr (**f**), n-Pr (**h**), t-Bu (**i**).

Intermediates with P–C bond proved to be unstable and we failed yet to synthesize them.

With the purpose of preparing intermediate VI PCl₃ was purified from the HCl impurity and was reacted with aldehydes. But under these conditions no formation of new phosphorus-containing products was observed. In ³¹P NMR spectrum of the reaction mixture only one signal at δ_P 220 ppm was observed corresponding to the phosphorus atom in compound Ia.

While performing the reaction between compounds **Ia** and **IIa** in the presence of catalytic amounts of tertiary amine the result of interaction crucially depended on the order of mixing the reagents. The addition of 3–4 drops of PCl₃ to a mixture of aldehyde and amine caused violent polymerization of compound **IIa** and no formation of organophosphorus compounds was observed. Addition of the rest amount of PCl₃ did not result in the temperature rise. After removing PCl₃ in a vacuum paraldehyde **XXIVa** was obtained in a high yield.

At a slow addition of aldehyde **IIa** to a mixture of PCl_3 with the catalytic amount of tertiary amine like triethylamine, *N*,*N*-dimethyl- and *N*,*N*-diethylanilines, pyridine, and 2,6-diethylaniline a strongly exothermic

process was observed. In ³¹P NMR spectrum taken 2 h after mixing the reagents three signals at δ_P 220, 178.1, and 177.8 ppm were present. The intensity ratio of the latter two was 3 : 1. Signals at 178.1 and 177.8 ppm correspond to a phosphorus environment OPCl₂ in alkylphosphorodichloridites [34, 35]. Therefore it was concluded that both these signals correspond to the same intermediate **VIa**.

$$\frac{PCl_3 + nRCHO}{I} \rightleftharpoons \frac{(RCHClO)_nPCl_{3-n}}{VI-VIII}$$

VI, n = 1, R = Me (a), *n*-Pr (b), *i*-Pr (c); **VII**, n = 2, R = Me (a); **VIII**, n = 3, R = Me (a).

In 6 h after mixing of the reagents ratio PCl₃: VIa makes up 1.4 : 1 from the integral intensity of these signals and further it doesn't practically change. ¹H NMR spectra of the mixture recorded 5 h after the beginning of the reaction show that compounds IIa, XXIVa, and VIa are presented in 1 : 9 : 40 ratio.

After removing PCl₃ and the insignificant admixture of acetaldehyde in a vacuum of water-jet pump, the residue was distilled in a vacuum from the Arbuzov flask or from the flask equipped with the 10-15 cm Vigreux column. A mixture containing compounds **VIa** and **XXIVa** in 5 : 1 ratio was obtained. In ³¹P NMR spectrum of this mixture two signals at δ_P 178.1 and 177.8 ppm corresponding only to phosphorus atom in the intermediate **VIa** were observed. ¹³C NMR spectrum contained the signals at δ_C (ppm): 19.89 s (Me), 97.5 s (CH) belonging to **XXIVa** and at 24.88 s (Me), 86.06 d (²*J*_{PC} 10.6 Hz, CH) attributed to **VIa**.

For the successful synthesis of compounds **VIa-VIc** the best ratio of starting substances (PCl₃, aldehyde, and tertiary amine) is 1 : 1 : 0.03-0.05. Aldehyde is slowly added dropwise under the intense stirring to a mixture of purified PCl₃ and amine at -5 to 0°C. Compounds **VIb,VIc** were isolated in a pure state by vacuum distillation. They are stable and can be stored in a sealed ampule at room temperature for several months. The structure of intermediates **VI** was confirmed by their complete elemental analysis, ¹H, ¹³C, and ³¹P NMR spectra (see the table), and chemical transformations.

When the amount of aldehyde involved in the reaction was increased further substitution of chlorine atoms in PCl₃ took place. While performing the reaction of PCl₃ with acetaldehyde in the presence of 2,6-dimethylpyridine in 1 : 2 : 0.01 ratio ³¹P NMR

~		δ, ppm (ⁿ J _{HH} , ⁿ J _{PH}					^п <i>J</i> _{HH} , ^{<i>n</i>} <i>J</i> _{PH} и ^{<i>n</i>} <i>J</i> _{PC} , Н	^{<i>n</i>} J _{PC} , Hz)		
Comp. no.	R ¹	\mathbb{R}^2	R ³	^m E	E^{1}	E^2	E ³	E^4	E^5	δ _P , ppm
VIa	Cl	Cl	CH ₃	¹ H	_	6.38 d.q (5.6, 13.9)	1.81 d 24.88 s	_	-	178.1 177.7
VIb	Cl	Cl	<i>p</i> -Pr	¹³ C ¹ H	-	86.06 d (10.6) 6.35 d.t (6.5, 15.0)	2.1 d.t (6.5, 7.5)	1.55 sextet (7.5, 7.5)	0.94 t (7.5)	180.42 180.83
VIc	Cl	Cl	CH(CH ₃) ₂	¹ H	-	6.13 d.d (3.8, 6.7)	2.2 heptet (3.8, 6.7)	1.06 d, 1.08 d (6.7)	-	179.61 179.24
				¹³ C		94.4 d (10.0)	36.87 s	17.27 s, 16.63 s		
VId	Cl	Cl	CCl ₃	¹ H	-	6.33 d (11.5)	-	_	-	184
VIIA	CI	OCHCICH ₃	CH ₃	¹³ C	_	84.66 d, 84.56 d (8.2)	27.66 s, 27.51 s	_	_	166.32 162.97 162.43
VIIb	Cl	CCl ₃ CH ₂ O	HC(CH ₃) ₂	$^{1}\mathrm{H}$	4.1 d (5.0)	6.14 d.d (4.0, 10.0)	2.1 heptet (4.0, 7.0)	0.9 d (7.0)	-	164.0 161.0
VIIIa	OCHCICH 3	OCHClCH ₃	CH ₃	¹ H ¹³ C	_	6.00–6.15 m 84.11–84.5 m	1.81 d (5.6) 27.56–27.77 m	-	_	145.85 138.82
VIIIb	CCl ₃ CH ₂ O	CCl ₃ CH ₂ O	HC(CH ₃) ₂	¹ H	4.1 d (5.0)	4.95 d.d (5.0, 9.0)	1.92–2.17 m	0.95 d (6.3)	-	133.0
VIIIc	PhO	PhO	HC(CH ₃) ₂	$^{1}\mathrm{H}$	6.90–7.15 m	5.6 d.d (4.5, 9.0)	1.93 d. гепt (4.5, 6.5)	0.9 d (6.5)	_	138.0 141.0
VIIId	CCl ₃ CH ₂ O	OCHCl(CH ₃) ₂	HC(CH ₃) ₂	$^{1}\mathrm{H}$	4.2 d (5.0)	5.95–6.25 m	1.95–2.19 m	1.0 d (6.5)	_	139.0 142.0
VIIIe	CCl ₃ CH ₂ O	OCHClCH ₃	CH ₃	$^{1}\mathrm{H}$	4.1 d (5.0)	5.96–6.28 m	1.85 d (6.5)	_	-	138.0 141.0
VIIIf		~ 0	$CH(CH_3)_2$	$^{1}\mathrm{H}$	6.70–7.05 m	5.5 d.d	1.93 d. hept	0.9 d	-	133.0
				¹³ C	109.3 s 120.5 s 142.3 d (6.5)	(4.5, 9.0) 88.5 d (6.5)	(4.5, 6.5) 33.5 s	(6.5) 13.5 s		
VIIIg			CH₃	¹ H ¹³ C	6.85–7.15 m 110.0 s, 120.5 s, 142.0 d (6.3)	5.4 d.q (6.3, 7.5) 80.8 d (7.5)	1.37 d (6.3) 24.0 s	_	-	133.1
VIIIi			C(CH ₃) ₃	¹ H	6.75–7.10 m	5.3 d (9.0)	_	0.9 s	_	133.0

¹H, ¹³C, and ³¹P NMR data of primary intermediates R¹R²POCHCIR³

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spectrum of reaction mixture 26 h after mixing of reagents $(-5^{\circ}C)$ contained three sets of signals: 220.0, and 178.1, 177.8 (ratio of intensities of the latter two was 3 : 1), and 163.3, 162.95, 162.43 ppm (3 : 2 : 1 ratio). As it was shown above, first three signals correspond to phosphorus atom in PCl₃ and intermediate VIa. Chemical shifts of the third set of signals correspond to a phosphorus environment O₂ClP(III) in dialkylphosphorochloridites [34, 35]. Therefore these three signals were attributed to phosphorus atom in the intermediate VIIa. Integral intensities of signals show that PCl₃ : VIa : VIIa ratio in the mixture is approximately makes up 1:8:11. After careful evacuating volatile products at room temperature and the residual pressure 0.02 mm into a trap cooled with liquid nitrogen the ³¹P NMR spectrum of the residue remained in the flask contained practically only the set of signals corresponding to compound VIIa. In the ¹H NMR spectrum the protons of methyl groups give a doublet at δ 1.83 ppm ($J_{\rm HH}$ 6.4 Hz), and the methine group protons give a multiplet at δ 6.1 ppm. It is shifted upfield as compared to the methine proton signal in the intermediate VIa (δ 6.38 ppm). ¹³C NMR spectrum contains two upfield singlets at $\delta_{\rm C}$ 27.66 and 27.51 ppm belonging to nonequivalent carbon atoms of two methyl groups and two downfield doublets at δ_C 84.66 ppm (${}^{2}J_{PC}$ 8.2 Hz) and 84.56 ppm (${}^{2}J_{PC}$ 5.3 Hz) corresponding to methine carbon atoms. The structure of intermediate VIIa is confirmed also by satisfactory elemental analysis and its oxidation to the corresponding phosphate. The mixture collected in the trap according to NMR spectral data consists of PCl₃, trimer XXIVa, and intermediate VIa.

At the attempts to distil compound **VIIa** in a vacuum it gradually decomposes to give volatile products. ¹H and ³¹P NMR spectra of the decomposition products (taken at -10° C) collected in the trap cooled with liquid nitrogen show that they are compounds **Ia**, **IIa**, and **VIa**. Special experiments showed that at prolonged heating in a vacuum to 100° C intermediate **VIa** completely decomposed to PCl₃ and aldehyde.

At further increase in the amount of aldehyde the substitution of chlorine atoms at P(III) becomes non-selective, and a series of products with various degree of substitution of chlorine atoms with 1-chloroethoxy group is formed. At performing the reaction between compounds **Ia**, **IIa**, and **XVII** at 1 : 4 : 0.02 ratio at -5° C in ³¹P NMR spectrum of reaction mixture taken

24 h after mixing of reagents besides the signals of phosphorus nuclei of the compounds VIa and VIIa two new signals at $\delta_{\rm P}$ 146.9 and 138.7 ppm were observed in 1:5 ratio. These values of chemical shifts correspond to a phosphorus environment O₃P(III) in trialkyl phosphites [34, 35]. Therefore they were attributed to one more intermediate VIIIa, namely, to tri(1-chloroethyl) phosphite. The ratio of compounds VIa, VIIa, and VIIIa in the reaction mixture was 1 : 9 : 14. Thus intermediate VIIIa is the main component of the mixture. New doublet at δ 1.81 ppm $(J_{\rm HH} 5.6 \text{ Hz})$ in the ¹H NMR spectrum of a mixture was attributed to the methyl group protons, and the signal of methine group protons overlapped with the multiplet of methine protons from compound VIIa at δ 6.11 ppm. In the ¹³C NMR spectrum new multiplets at δ_C 27.58–27.77 and δ_C 84.11–84.52 ppm were found. They were attributed to the methyl and methine group carbon atoms of compound VIIIa respectively.

At the attempt to distil this mixture in a vacuum it rather rapidly decomposes to give the intermediate **VIa**, PCl₃ and acetaldehyde. Note that the previously suggested isomerization [2, 3] of compound **VIIIa** to P(IV) derivative does not take place. Instead it decomposes while heating to give the starting products.

Hence, by the reaction of PCl₃ with aldehydes in the presence of catalytic amounts of tertiary amine three types of primary intermediates VIa, VIIa, and VIIIa were synthesized for the first time. They differ from one another by the degree of substitution of chlorine atoms in PCl₃ with 1-chloroalkoxy group. The formation of intermediates VI-VIII is a reversible process. The accumulation of 1-chloroalkoxy groups at P(III) atom decreases the stability. Intermediates VIIa and VIIIa exist only in the cold. At room temperature and above it, and at removing the decomposition products in a vacuum they completely convert in starting compounds. Intermediates VIa-VIc can be distilled in a vacuum. They may be stored for a long time in sealed ampules and decompose only at prolonged heating in a vacuum.

The reaction of P(III) chlorides with chloral must be considered specially. Chloral is an aldehyde whose carbonyl oxygen exhibits decreased nucleopilicity due to the effect of three electron-acceptor chlorine atoms. As known, P(III) chlorides exhibiting electrophilic reactivity under the conditions of acidic catalysis do not react with chloral [15, 16]. We suggested that chloral molecule activated with tertiary amine would react at least with such active electrophile as PCl₃. It really occurred that under considerably mild conditions (0 to -5° C) chloral reacts with PCl₃ in the presence of catalytic amount of tertiary amine (1 : 1 : 0.03) to give primary intermediate **VId**.

$$CCl_{3}CHO + PCl_{3} \stackrel{B}{\rightleftharpoons} CCl_{3}CHOPCl_{2}$$

$$\downarrow \\Cl$$
VId

Five hours after mixing of reagents ³¹P NMR spectrum of reaction mixture contained three signals at 220, 184, and 164 ppm in 1 : 8 : 1 ratio. Intermediate **VId** occurred to be the main reaction product, and the signal with δ_P 184 ppm was attributed to its prosphorus atom. In the ¹H NMR spectrum only one doublet at 6.33 ppm (J_{PH} 11.25 Hz) corresponding to methine proton was observed. Another P(III) chlorides showing electrophilic reactivity under the analogous conditions did not show the signs of reaction with chloral.

Another method for preparing primary intermediates is connected with the use of alkyl vinyl ethers. Alkyl vinyl ethers were mixed at room temperature with catechol chlorophosphite, and isobutyric aldehyde was added to this mixture. Preliminary purification of catechol chlorophosphite from the HCl admixture was not carried out. It occurred that in the ¹H NMR spectrum of the distilled product **VIIIf** multiplets at 3.9 and 1.0 ppm were observed. Their intensity varied from the experiment to experiment. These signals were attributed to the products of polymerization of alkyl vinyl ethers.



VIII, R = i-Pr (f), Me (g), *n*-Pr (h), *t*-Bu (i).

With the purpose of removing these admixtures catechol chlorophosphite after primary treatment with alkyl vinyl esters was distilled into the reaction flask, and then alkyl vinyl ethers and aldehyde were added. In this way compound **VIIIf** was synthesized. After distillation it did not contain admixtures except 15% of starting catechol chlorophosphite. The improved protocol was used for the synthesis of new intermediates **VIIIg–VIIIi** from catechol chloro-

phosphite. Compound **VIIIi** was isolated pure by vacuum distillation (see the table). Other substances were studied without purification after removing volatile substances in a high vacuum (see the table).

Diphenyl posphorochloridite **Ic** reacts with isobutyric aldehyde analogously.

According to ³¹P NMR data the ratio of compounds **VIIIc** (δ_P 130 ppm) and **Ic** (δ_P 156 ppm) after the establishment of the equilibrium was 10 : 1. For the confirmation of structure of the intermediate the aldehyde was quickly removed from the ccoled reaction mixture in a high vacuum, and ¹H NMR spectrum of the residue was recorded (see the table).

By an example of the reactions of catechol chlorophosphite we have established the character of dependence of conversion of starting products and the stability of the intermediates on the structure of aldehyde. According to ³¹P NMR data at catechol chlorophosphite: RCHO : alkyl vinyl ether ratio 1 : 2 : 1 the conversion of chlorophosphite was 58% when R = Me, 65% when R = n-Pr, and 75% when R = i-Pr. At the increase in the amount of aldehyde involved in the reaction the conversion of catechol chlorophosphite sharply increased. At 1 : 7 : 2 ratio of starting substances the conversion of catechol chlorophosphite reached 100% when R = i-Pr and t-Bu, and 90% when R = Me, and *n*-Pr. Intermediate VIIIi was distilled without decomposition. According to ³¹P NMR data the catechol chlorophosphite content in distillate was 15% at R = i-Pr, 40% at R = n-Pr, and 50% at R = Me. These data show that the stability of the intermediates VIII increases with the increase in donor properties of the aldehyde fragment.

It was important also to establish the character of the effect of substituents at P(III) on the stability of primary intermediates **VI–VIII**. The above data concerning the two direct methods of synthesis of the intermediates **VI**, **VIIb**, and **VIIIf–VIII** show that introduction of more electropositive substituents like 1-chloroethoxy, phenoxy, or phenylene-1,2-dioxy group instead of chlorine atoms on P(III) decreases the stability of these compounds. As known, tris(2,2,2trichloroethyl)phosphite does not enter the Michaelis– Arbuzov reaction even with such strong electrophiles as α -chloroethers [36]. Evidently trichloroethoxy group is sufficiently strong acceptor of electrons, and nucleophilicity of P(III) sharply decreases. We suggested that introduction of 2,2,2-trichloroethoxy groups to P(III) atom must lead to an increase in the stability of the primary intermediate.

Really, in the reaction of bis(2,2,2-trichloroethyl) phosphorochloridite **Id** with aldehyde in presence of alkyl vinyl ethers as a catalyst intermediate **VIIIb** was obtained. It is stable at room temperature for a long time.

$$(CCl_{3}CH_{2}O)_{2}PCl + i\text{-}PrCHO \rightleftharpoons (CCl_{3}CH_{2}O)_{2}POCHPr\text{-}i$$

$$\downarrow \\ Cl$$
Id
VIIIb

Meanwhile, heating in a vacuum leads to its decomposition with the liberation of aldehyde molecule before reaching the boiling point. Therefore compound VIIIb was identified as a crude product after removing all volatile admixtures in a high vacuum. Its spectral characteristics are presented in the table. This substance was also synthesized by the third indirect method by means of the reaction of intermediate VIb with 2,2,2-trichloroethanol in the presence of tertiary amine. Spectral characteristics of compound VIIIb obtained by different methods are identical. All the attempts to prepare primary intermediates by direct method from ethyl phosphorodichlorite and ethyldichlorophosphine failed. The reaction mixture was a very viscous liquid, and in its NMR spectra the signals belonging to P(III) atoms and the protons of CH₃CH·(Cl)OP(III) fragment were absent. Evidently, primary intermediates contain-ing EtO[MeCH(Cl)O]P(III) and Et[MeCH(Cl)O]P(III) fragments are still less stable than compounds VIIa and **VIIIa**. Another side of the problem is that P(III) chlorides which can exhibit electrophilic as well as nucleophilic properties in the reactions with the same reagent, for example, nonsubstituted dialkyl phosphorochloridites, react with aldehydes to give polymeric products [22]. The nucleophilicity of P(III) atom in bis-(2,2,2-trichlo-roethyl)- Ic and di(1-chloroethyl) chlorophosphites VIIa is evidently decreased due to the effect of two electron-acceptor 2,2,2-trichloroethyl or 1-chloroethyl groups. They exhibit only electro-philic properties in the reactions with aldehydes leading to the formation of intermediates VIIIb and VIIIa. At the same time in ethyl (1-chloroethyl) phosphorochloridite VIIc and (1-chloroethyl) ethylphosphonochloridite VIId the nucleophilicity of P(III) atom is sufficiently high to react with aldehydes analogously to nonsubstituted dialkyl phosphorochloridites.

EtO(MeCHClO)PCl Et(MeCHClO)PCl VIIc VIId

Hence, by introduction of several chlorine atoms into the alkyl groups of dialkyl phosphorochloridites we managed to direct the reaction towards the formation of primary intermediates **VIIIa**, **VIIIb** instead of the polymeric products.

Analogous results were obtained also by replacement of ethoxy group in ethyl phosphorodichloridite by 2,2,2-trichloroethoxy one. At the reaction of 2,2,2trichloroethyl phosphorodichloridite **Ie** with the twofold excess of isobutyraldehyde in the presence of alkyl vinyl ethers the substitution of the first, and then of the second chlorine atom with 1-chloroalkoxyl group takes place. Hence, after 24 h of keeping the reaction mixture at room temperature its ³¹P NMR spectrum contains three signals at δ_P 164, 161 (intensity ratio 2 : 1) and at δ_P 179 ppm.



First two of them correspond to phosphorus environment O₂ClP(III) [34, 35], in dialkyl phosphorochloridites. Therefore they were attributed to phosphorus atom in the intermediate VIIb. Third signal in the spectrum belongs to the phosphorus atom of starting dichlorophosphite Ie. From the integral intensity of signals the ratio of compounds Ie and VIIb is 1 : 1. After 6 days in ³¹P NMR spectrum of reaction mixture weak signals at δ_P 164, 161, and 22 ppm and intensive signals at δ_P 142 and 139 ppm (ratio 3 : 1) were observed. First two signals of these mixtures are attributed to phosphorus atom in compound VIIb. the third signal, to P(IV) atom, and δ_P values of the last two signals correspond to phosphorus environment O₃P(III) [34, 35] in trialkyl phosphites. Therefore they were attributed to phosphorus atom in the intermediate VIIId. Analogous intermediate VIIIe was synthesized from acetaldehyde. Spectral characteristics of compounds VIIId, VIIIe are listed in the table.

Finally, intermediates **VIIIj**, **VIIIk** containing two nonsubstituted alkoxy groups on P(III) were prepared by indirect method reacting compound **VIc** with the corresponding alcohols in the presence of tertiary amine. It turned out that they are stable in strongly diluted ether solutions at 0 to -5° C. Their structure was confirmed by NMR spectra and by oxidation to the corresponding phosphates. At removing of solvent or increasing the temperature to 20–25°C an exothermic

reaction leading to the formation of viscous liquid takes place. In NMR spectra of the latter signals corresponding to Me₂CHCH(Cl)OP(III) fragment were absent.

The above data also permit to come to the conclusion that the stability of primary intermediates increases with the increase in electron-acceptor properties of substituents at P(III) and the donor properties of aldehyde fragment.



The mechanism of catalysis of the reaction of P(III) chlorides with aldehydes with tertiary amines or alkyl vinyl ethers we did not study specially. But it may be suggested that the soft interaction of nucleophile with carbonyl carbon atom increases nucleophilic properties of the carbonyl oxygen. Carbonyl group is activated and simultaneously its electrophilic center is protected from the addition of the second aldehyde molecule. The aldehyde molecule **XXV** activated with nucleophile reacts with P(III) chlorides through the charge separation **XXVI** or the synchronic cyclic electron transfer **XXVII** to give the first intermediate with the liberation of catalyst.

EXPERIMENTAL

NMR spectra were recorded on spectrometers 7.0 T IBM/Bruker AF 300 (300 MHz ¹H, 75.5 MHz ¹³C, 121.5 MHz ³¹P), Tesla BS-567A (100 MHz ¹H), and Bruker MSL-400 (162 MHz ³¹P). Chemical shifts of hydrogen and carbon are given with respect to TMS, and of phosphorus, with respect to 85% phosphoric acid.

Removing HCl impurity from P(III) chlorides. *a. Treating with tertiary amine.* Commercial PCl₃, 25.5 g (0.186 mol), was mixed at room temperature with 3.5 g (0.029 mol) of *N*,*N*-dimethylaniline, and PCl₃ was distilled directly into the reaction flask. For this purpose another nitrogen-containing organic bases like pyridine, 2,6-dimethylpyridine, and triethylamine can be used. b. Treating with alkyl vinyl ethers. Catechol chlorophosphite, 10 g (0.06 mol), was cooled to 10°C and 4.13 g (0.06 mol) of ethyl vinyl ether was added. α -Chloroether obtained and excess ethyl vinyl ether were removed in a vacuum, and catechol chlorophosphite was distilled in a vacuum directly into the reaction flask. Another alkyl vinyl ethers like vinyl butyl and vinyl isobutyl ethers may be used.

Reactions of P(III) chlorides with aldehydes. *a. Reaction of purified PCl₃ with acetaldehyde in the absence of catalyst.* Acetaldehyde, 3.2 g (0.073 mol), was added dropwise under the intensive stirring to 10 g (0.073 mol) of phosphorus trichloride twice treated with *N,N*-dimethylaniline at -5° C. No increase in temperature was observed. The mixture obtained was kept for 27 h in the freezer. In ³¹P NMR spectrum only one singlet at 220 ppm corresponding to PCl₃ was observed.

b. Reaction of PCl₃ with aldehydes in the presence of tertiary bases. Phosphorus trichloride, 7.55 g (0.055 mol), was added dropwise under the intensive stirring to a mixture of 7.26 g (0.168 mol) of acetaldehyde and 0.246 g (0.0017 mol) of *N*,*N*-diethylaniline at -5 to 0°C. The addition of the first three drops of PCl₃ caused strong heat evolution and the temperature of reaction mixture rose to 25°C. At the addition of the rest amount of phosphorus trichloride at 0°C no increase in temperature was observed. ¹H NMR spectrum, δ , ppm: 1.29 d (³J_{HH} 5.1 Hz, 3H, Me), 4.94 q $({}^{3}J_{\rm HH}$ 5.1 Hz, 1H, CH). 13 C NMR spectrum, $\delta_{\rm C}$, ppm: 19.89 s Me, 97.5 s CH (paraldehyde). 31 P NMR spectrum, $\delta_{\rm P}$, ppm: 220 (PCl₃). PCl₃ was removed in a vacuum (120 mm) and the residue was distilled to give 4.1 g of paraldehyde.

1-Chloro 2-methylpropyl phosphorodichloridite VIc. To a mixture of 10 g (0.073 mol) of PCl₃ and 0.139 g (0.0036 mol) of 2,6-dimethylpyridine 5.26 g (0.073 mol) of isobutyraldehyde was added dropwise. The reaction mixture was kept for 18 h and diluted with 15 ml of anhydrous hexane. Insignificant amount of precipitate was filtered off, the solvent was removed, and the residue was distilled in a high vacuum to give 8.17 g (53%) of product **VIc**, bp 30°C (0.01 mm Hg), d_4^{20} 1.3029. Found, %: C 22.74, H 3.81; Cl 50.51; P 14.65. C₄H₈Cl₃OP. Calculated, %: C 22.91; H 3.82; Cl 50.83; P 14.79. NMR spectral data are listed in the table.

1-Chlorobutyl phosphorodichloridite VIb. This com-pound was obtained analogously from 19.53 g (0.142 mol) of PCl₃, 0.42 g (0.0028 mol) of *N*,*N*-diethylaniline, and 10.24 g (0.142 mol) of butyral-dehyde. Yield of product **VIb** 16.04 g (54%), bp 30–32°C (0.02 mm Hg), n_D^{20} 1.4821, d_4^{20} 1.2897. Found, %: C 23.13, H 4.02, Cl 50.67, P 14.60. C₄H₈Cl₃OP. Calculated, %: C 22.91, H 3.82, Cl 50.83, P 14.29. NMR spectral data are listed in the table.

1-Chloroethyl phosphorodichloridite VIa. Vacuum distillation of the reaction mixture prepared from 18.36 g (0.134 mol) of PCl₃, 0.4 g (0.0027 mol) of *N*,*N*-diethylaniline, and 5.9 g (0.134 mol) of acetaldehyde gave 12.8 g of a mixture of product **VIa** and paral-dehyde **XXVIIa** (3:1 according to ¹H NMR spectrum). NMR spectral data are listed in the table. 3 g of this mixture was heated at 20–90°C in a vacuum and volatile products were collected in a trap cooled with liquid nitrogen. ¹H NMR spectrum of condensate, δ , ppm: 2.1 d, 9.7 q, **IIa**; 1.29 d, 4.94 q, **XVIIa**. ³¹P NMR spectrum, δ_P , ppm: 220, PCl₃.

1,2,2,2-Tetrachloroethyl phosphorodichloridite VId. Chloral, 17.38 g (0.118 mol), was added dropwise at -5° C to a mixture of 16.2 g (0.118 mol) of PCl₃ and 0.35 g (0.0024 mol) of *N*,*N*-diethylaniline. The reaction mixture was stirred for 1 h at this temperature. Data of ¹H and ³¹P NMR spectra of the crude product **VId** after removing volatile components in a vacuum are presented in the table.

Di(1-chloroethyl) phosphorochloridite VIIa. Acetaldehyde, 5.52 g (0.1256 mol), was added dropwise at -5° C to a mixture of 9.33 g (0.068 mol) of PCl₃ and 0.025 g (0.0017 mol) of *N*,*N*-diethylaniline. The reac-tion mixture was kept for 26 h at -5° C, its ³¹P NMR spectrum was taken, and volatile components were distilled in high vacuum in a trap cooled with liquid nitrogen. According to ³¹P, ¹H, and ¹³C NMR spectra (see the table) the residue is sufficiently pure product **VIIa.** Found, %: Cl 47.85, P 13.34. C₄H₈Cl₃O₂P. Calculated, %: Cl 47.23, P 13.74.

Crude compound **VIIa**, 3 g, was heated gradually to 70°C at the residual pressure 0.01 mm. Progressive increase in residual pressure to 0.1 mm took place, and the distillation flask remained almost empty. In ³¹P NMR spectrum of volatile compounds collected in the nitrogen-cooled trap signals with δ_P 220 and 178.1, 177.9 ppm were observed at -10°C. They were attributed to phosphorus atom in PCl₃ and the compound **VIa** respectively. In ¹H NMR spectrum of this preparation signals were present belonging to acetaldehyde [δ 2.1 ppm, d (CH₃CO); 9.7 ppm, q (CHO)] and to compound **VIa** [δ 1.81 ppm, d.d (CH₃); 6.38 ppm, d.q (PCH)]. Weak signals of trimer protons were also observed.

Tri(1-chloroethyl) phosphite VIIIa. Acetaldehyde, 15.51 g (0.352 mol), was added dropwise with intensive stirring at -5 to 0°C to a mixture of 12.12 g (0.088 mol) of PCl₃ and 0.43 g (0.0044 mol) of 2.6dimethylpyridine. After 24 h of keeping at -5°C ¹H, ¹³C, and ³¹P NMR spectra of this mixture at the same temperature were registered (see the table). Crude product, 3 g, was gradually heated in a high vacuum at the progressive increase in temperature from 23 to 80°C. Volatile products were collected in a trap cooled with liquid nitrogen. ³¹P NMR spectrum of a mixture from the trap, δ_{P} , ppm: 220 (PCl₃), 178.1, 177.8 (VIa). ¹H NMR spectrum, δ , ppm: IIa: 2.1 d (MeCO, ${}^{3}J_{HH}$ 3 Hz), 9.7 q (CH, ${}^{3}J_{\text{HH}}$ 3 Hz); paraldehyde: 1.29 d (CH₃, ${}^{3}J_{\text{HH}}$ 5.1 Hz), 4.9 q (CH, ${}^{3}J_{\text{HH}}$ 5.1 Hz); VIa: 1.81 d, (Me, $J_{\rm HH}$ 5.6 Hz); 6.38 d.q (CH, ${}^{3}J_{\rm HH}$ 5.6 Hz, ${}^{2}J_{\rm PH}$ 13.0 Hz).

(1-Chloro-2-methylpropyl) diphenyl phosphite VIIIc. Isobutyric aldehyde, 1.87 g (0.026 mol), was added dropwise at $0-1^{\circ}$ C to a mixture of 6.45 g (0.026 mol) of diphenyl phosphorochloridite and 0.053 g (0.00052 mol) of triethylamine. After keeping for four days at room temperature an insignificant amount of precipitate was filtered off. Volatile compounds were removed in a high vacuum. In ³¹P NMR spectrum of reaction mixture two signals at δ_P 130 and 156 ppm in 10 : 1 ratio (see the table) were observed.

Catechol (1-chloro-2-methylpropyl) phosphite VIIIf. Catechol chlorophosphite, 17.79 g (0.10 mol), was cooled to 10°C, and 14.7 g (0.2 mol) of ethyl vinyl ether was added dropwise to it. Isobutyraldehyde, 50.47 g (0.7 mol), was added dropwise to a mixture obtained. The resulting mixture was kept at room temperature for three days. After that volatile products were removed in a high vacuum to give 24.5 g of crude product. Its ³¹P NMR spectrum contained one signal at 133 ppm (see the table), $n_{\rm D}^{20}$ 1.5220, d_4^{20} 1.2459. The conversion of catechol chlorophosphite was 100%. At the distillation in high vacuum practically one fraction was collected. Its ³¹P NMR spectrum contained two signals at δ_P 174 and 133 ppm in 1 : 5.7 ratio. This means that 15% of compounds VIIIf decomposes to catechol chlorophosphite.

Catechol (1-chloro-2,2-dimethylpropyl) phosphite VIIIi. Ethyl vinyl ether, 2.5 g (0.035 mol), was added dropwise to 6.14 g (0.035 mol) of pyrocatechol chlorophosphite cooled to 10°C, and then to this mixture 6.06 g (0.07 mol) of trimethylacetaldehyde was added dropwise. After 3 days volatile products were removed in a vacuum. The distillation in a high vacuum gave 6 g (77%) of product **VIII**i, bp 74–75°C (0.02 mm Hg), n_D^{20} 1.5168, d_4^{20} 1.2159. Found, %: C 50.52; H 5.29; Cl 13.85; P 11.61. C₁₁H₁₄ClO₃P. Calculated, %: C 50.67; H 5.37; Cl 13.60; P 11.88.

Catechol (1-chlorobutyl) phosphite VIIIh. Ethyl vinyl ether, 4.3 g (0.06 mol), was added drop-wise to 5 g (0.03 mol) of catechol chlorophosphite cooled to 10°C, and 15.14 g (0.21 mol) of butyraldehyde was added dropwise to this mixture. After 3 days two signals at δ_P 174 and 133 ppm in 1 : 9 ratio were observed in ³¹P NMR spectrum. Thus the conversion of catechol chlorophosphite was 90%.

Catechol (1-chloroethyl) phosphite VIIIg. Ethyl vinyl ether, 4.3 g (0.06 mol) was added dropwise to 5 g (0.03 mol) of catechol chlorophosphite as in the previous experiments, and then 9.25 g (0.21 mol) of acetaldehyde was added dropwise to this mixture. Two signals at δ_P 174 and 133 ppm in 1 : 9 ratio were observed in ³¹P NMR spectrum. Thus the conversion of catechol chlorophosphite was 90%. After distillation of reaction mixture practically one fraction was obtained. Its ³¹P NMR spectrum contained the same two signals at 174 and 133 ppm in 1 : 1 ratio indicating about 40% decomposition of compound **VIIIg**.

(1-Chloro-2-methylpropyl) bis(2,2,2trichloroethyl) phosphite VIIIb. a. Bis(2,2,2trichloroethyl) phosphorochloridite, 19 g (0.052 mol), was cooled to 10°C and 7.5 g (0.104 mol) of ethyl vinyl ether was added. Then 18.7 g (0.26 mol) of isobutyraldehyde was added dropwise to this mixture. After 5 days volatile substances were removed in a vacuum, and 18.1 g of crude product was obtained. Its ³¹P NMR spectrum besides the intense signal at δ_P 138 ppm contained also weak signal at 165 ppm (see the table).

b. 1-Chloro-2-methylpropyl phosphorodichloridite, 9.7 g (0.046 mol), was added dropwise at -2 to -4° C to a solution of 13.89 g (0.093 mol) of triethylamine and 9.37 g (0.093 mol) of trichloroethanol in ether. After stirring for 1 h at this temperature amine hydrochloride was filtered off, and volatile compounds were removed in a vacuum. ³¹P NMR spectrum of the residue contained intensive signal at δ_P 138 ppm and weak signals at 165 and 22 ppm. In the course of prolonged keeping no change in the intensity of signals is observed. ¹H NMR spectra of compounds obtained by different methods are identical.

Di(1-chloroethyl) (2,2,2-trichloroethyl) phosphite VIIIe. 2,2,2-Trichloroethyl phosphorodichloridite, 29.8 g (0.119 mol), was cooled to 10°C and 17.2 g (0.24 mol) of ethyl vinyl ether was added to it. After that 36.7 g (0.83 mol) of acetaldehyde was added dropwise to the mixture obtained. After 5 days volatile substances were removed in a vacuum. In ³¹P NMR spectrum of reaction mixture signals at δ_P 141 and 138, 163, and 22 ppm were present. First two of them correspond to P(III) atom in compound **VIIIe**. Total integral intensity of the first two signals relates to the intensities of the second and third signals as 8 : 1 : 2. The description of ¹H NMR spectrum of compound **VIIIe** is presented in the table.

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