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Reaction of P(III) Chlorides with Aldehydes: II.[1] Reaction of Primary Intermediates with Aprotic Nucleophiles: Ethylene Oxide, Acetals, Trialkyl Orthoformates, and Trialkyl Phosphites

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Abstract—Structure of primary intermediates of the reaction of P(III) chlorides with aliphatic aldehydes was confirmed by their reactions with such aprotic reagents like ethylene oxide, trialkyl phosphites, acetals, and trialkyl orthoformates. Principle difference in the reactions of these nucleophiles with intermediates containing active chlorine atom at P(III) and those not containing was established. The former as well as all the other P(III) chlorides react directly with nucleophiles, while the latter slowly decompose into aldehyde and P(III) chloride, and the latter reacts with the nucleophile.

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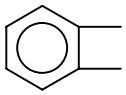
In the previous report we have described three synthetic procedures for the preparation of three types of intermediates in the reactions of electrophilic P(III) chlorides **I** with aliphatic aldehydes **II**. These intermediates differ in the nearest surrounding of P(III) atom containing Cl_2OP(III), ClO_2P(III) and O_3P fragments [1]. Considering the difference in chemical properties of these intermediates we have divided them in two types , i.e., the substances **III** containing active chlorine at P(III) atom and compounds **IV** which do not contain it.

Cl(X)POCHClR — **III**

$R^1O(R^2O)POCHClR$ — **IV**

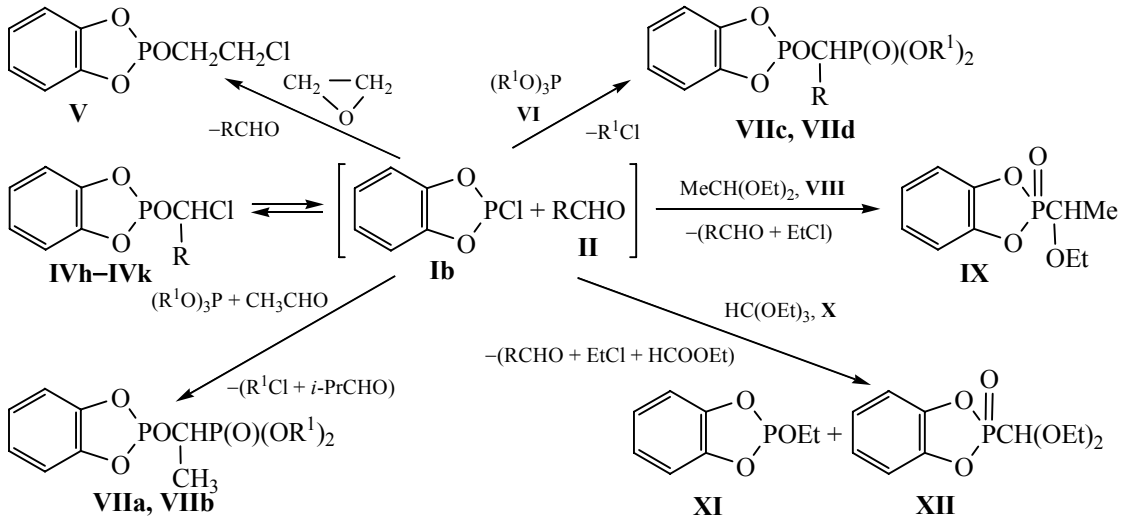
III, X = Cl, R = Me (**a**), Pr (**b**), *i*-Pr (**c**), CCl_3 (**d**); X = MeCHClO, R = Me (**e**); X = CCl_3CH_2O, R = *i*-Pr (**f**); **IV**, R = Me, $R^1 = R^2$ = MeCHCl (**a**); $R^2 = CCl_3CH_2$, R^1 = MeCHCl (**b**); R = *i*-Pr, $R^1 = R^2 = CCl_3CH_2$ (**c**); Ph (**d**); Me (**e**); Et (**f**); $R^1 = CCl_3CH_2$, R^2 = *i*-PrCHCl (**g**); $R^1 + R^2$ =  ; R = Me (**h**); *i*-Pr(**i**); Pr (**j**); *t*-Bu (**k**).

Compounds **III** are stable, in particular, when X = Cl, and they can be distilled in a vacuum without decomposition. Substances **IV** are less stable and especially under heating decompose to give the starting P(III) chloride and aldehyde. It can be suggested that such aprotic nucleophiles as alkene oxides, acetals, alkyl orthocarboxylates, and trialkyl phosphites will react with forming P(III) chloride shifting the equilibrium to the side of decomposition of intermediates **IV**. Intermediates of the first type **III** may react with them directly.

As is known, oxiranes react with all P(III) chlorides to give products of ring opening [2-7]. In these reactions the coordination number of phosphorus is retained. Depending on the reagent ratio it is possible to substitute step-by-step all chlorine atoms at P(III) with 2-chloroethoxy group. Acetals and alkyl orthocarboxylates react with P(III) chlorides with the cleavage of C–O bond. In all cases P(III) chlorides exhibit electrophilic properties and the primary process is the exchange of chlorine atoms at P(III) for the alkoxy groups [2, 9–12]. Since the intermediate P(III) acid esters, α-chloroethers, or chloroformals easily react with one another, the process usually finishes at the formation of P(IV) derivatives [2, 8–12].

[1] For communication I, see [1].

Among the intermediates of the second type **IV** compounds **IVh–IVk** turned out to be the most convenient for investigation. Results obtained while studying their reactions with the above-mentioned nucleophiles may be represented by the following scheme.



VII, R^1 = Me (**a**), Et (**b**); R = *i*-Pr, R^1 = Me (**c**), Et (**d**).

While mixing compound **IVi** with ethylene oxide in 1 : 1 ratio at 5°C a very weak heat evolution is observed (increase in temperature by 2°C). In ^{31}P NMR spectrum of the reaction mixture a new signal at δ_P 129 ppm appeared, and its intensity slowly grew. Only after 145 h this signal became the main one. The reaction product, i.e., 2-chloroethyl pyrocatechol phosphite **V**, was isolated in a pure state by vacuum distillation, and its structure was confirmed by ^{31}P and ^{1}H NMR spectra and by an authentic synthesis. The model reaction between pyrocatechol chlorophosphite **Ib** and ethylene oxide proceeds with heat evolution, and after 24 h in ^{31}P NMR spectrum of the reaction mixture one singlet at δ_P 129 ppm corresponding to phosphorus atom in compound **V** is observed. Constants and characteristics of ^{1}H NMR spectra of the product **V** obtained by different methods were identical.

In the nineteen sixties a great number of patents describing the reactions of carbonyl compounds activated with trialkyl phosphites **VI** with P(III) chlorides was claimed [13, 14]. We suggested that if intermediates **IV** are mixed with trialkyl phosphites the latter will react with the products of their decomposition according to the scheme of the reaction proceeding in the three-component system. Really, while adding trialkyl phosphite to intermediate **IVi** a slight heat evolution is observed. After 24 h ^{31}P NMR spectrum of the reaction mixture contained only two doublets of approximately equal intensity at δ_P 23 and 140 ppm corresponding to O_3P(IV)C and O_3P(III) surrounding of phosphorus, i.e., to phosphorus atoms in the product **VII**.

^{1}H NMR spectral characteristics of compounds **VII** are listed in the table.

It must be noted that compounds **VII** can be formed directly from the intermediates **IVh–IVk** as a result of bimolecular nucleophilic substitution.

With the purpose of disproofing this version we have carried out the reaction of intermediate **IVi** with triethyl phosphite **VIb** in the presence of four-fold excess of acetaldehyde **IIa**. Compound **VIIb** was obtained in a high yield. The latter does not contain the aldehyde fragment of the intermediate **IVi** indicating

Some ^{1}H, ^{13}C, and ^{31}P NMR data of phosphoryl compounds $R^1R^2P(O)R^3$

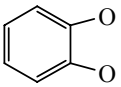
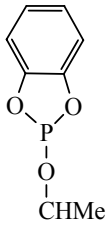
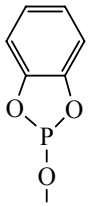
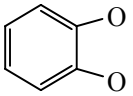
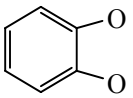
Comp. no.	R^1	R^2	R^3	δ, ppm (*J*, Hz)
V			OCH_2CH_2Cl	δ_H: 3.5 d.t (2H, CH_2OP, $J_{PH} = J_{HH}$ = 6.5), 3.8 t (2H, CH_2OP, J_{HH} 6.5), 6.91–7.20 m (4H, Ar); δ_P 129
VIIa	MeO		OMe	δ_H: 1.4 d (3H, Me, J_{HH} 7.0), 3.51 d (6H, OMe, J_{PH} 10.0), 6.57–6.83 m (4H, Ar); δ_P 23, 140
VIIc	MeO		OMe	δ_H: 0.63 и 0.70 d (6H, Me, J_{HH} 6.3), 3.55–3.85 m (1H, $\underline{CH}Me_2$), 3.50 d and 3.55 d (6H, OMe, J_{PH} 10.0), 1.64–1.87 m (1H, OCH), 6.65–6.87 m (4H, Ar); δ_P 23, 140
IX			$MeCHOCH_2Me$	δ_H: 0.88 t (3H, $OCH_2\underline{CH_3}$, J_{HH} 7.0), 1.43 d.d (3H, $CH\underline{CH_3}$, J_{PH} 18.5, J_{HH} 7.0), 3.47 q (2H, $O\underline{CH_2}CH_3$, J_{HH} 7.0), 4.00 d.q (3H, $\underline{CH}CH_3$, J_{PH} 3.5, J_{HH} 7.0), 6.59–6.88 m (4H, Ar); δ_P 46
XII			$CH(OCH_2Me)_2$	δ_H: 1.20 t (6H, $OCH_2\underline{CH_3}$, J_{HH} 7.0), 3.70 q (4H, $O\underline{CH_2}CH_3$, J_{HH} 7.0), 4.70 d (1H, PCH, J_{PH} 5.0), 6.50–6.82 m (4H, Ar); δ_P 46
XIV	MeO	MeOCHMe	MeO	δ_H: 1.55 d.d (3H, $CH\underline{CH_3}$, J_{PH} 18.0, J_{HH} 7.0), 3.20 s (3H, OCH_3), 3.50 d (6H, OCH_3, J_{PH} 10.0), 4.32–4.67 m (1H, CH); δ_P 25
XVb	MeO		$OCH(Cl)(CH_2)_2CH_3$	δ_H: 0.83 t (3H, $CH_2\underline{CH_3}$, J_{HH} 6.3), 1.09–1.30 m (3H, $CH\underline{CH_3}$), 1.32–1.54 m (2H, $\underline{CH_2}CH_3$), 1.80–2.00 m (2H, $\underline{CH_2}CH_2CH_3$), 3.37 s (3H, OCH_3), 3.65 d (3H, OCH_3, J_{PH} 10.0), 4.54–4.86 m (1H, PCH), 5.98–6.12 m (1H, POCH); δ_C: 11.2, 13.1 d (J_{PC} 12.0), 15.8, 40.6, 50.8, 56.9 d (J_{PC} 8.0), 71.7 d (J_{PC} 168.0), 72.0 d (J_{PC} 162.0), 72.3 d (J_{PC} 166.0), 86.9 d (J_{PC} 10.0); δ_P 25
XVc	MeO	MeOCHMe	$OCH(Cl)CH(CH_3)_2$	δ_H: 1.00 d (6H, $CH\underline{CH_3}$, J_{HH} 6.3), 1.41 d.d (3H, $PCH\underline{CH_3}$, J_{PH} 18.0, J_{HH} 7.0), 1.96–2.32 m (1H, $CH\underline{CH}CH_3$), 3.40 s (3H, OCH_3), 3.65 d (3H, OCH_3, J_{PH} 10.0), 4.47–4.70 m (1H, PCH), 5.95–6.27 m (1H, POCH); δ_P 25
XIXa	MeO	$CH(OMe)_2$	MeO	δ_H: 3.26 c (6H, $CHO\underline{CH_3}$), 3.61 d (6H, OCH_3, J_{PH} 11.0), 4.67 d (1H, POCH, J_{PH} 5.0); δ_P 16.4
XIXb	$MeCH_2O$	$CH(OCH_2Me)_2$	OCH_2Me	δ_H: 1.10 t (6H, $CH_2\underline{CH_3}$, J_{HH} 7.0), 1.17 t (6H, $CH_2\underline{CH_3}$, J_{HH} 7.0), 3.63 q and 3.70 q (4H, OCH_2, J_{PH} 7.0), 4.10 quntet (2H, POCH, J_{PH} 7.0, J_{PH} 7.0), 4.67 d (4H, OCH_2, J_{PH} 5.0); δ_P 16.8
XXb	$MeCH_2O$	$CH(OCH_2Me)_2$	$OCH(Cl)(CH_2)_2Me$	δ_H: 0.91 t (3H, $CH_2\underline{CH_3}$, J_{HH} 7.5), 1.17 t (6H, $OCH_2\underline{CH_3}$, J_{HH} 7.5), 1.31 t (3H, $POCH_2\underline{CH_3}$, J_{HH} 7.5), 1.40–1.56 m (2H, $CH_2\underline{CH_2}CH_3$), 1.82–2.12 m (2H, $\underline{CH_2}CH_2CH_3$), 3.51–3.90 m (2H, $O\underline{CH_2}CH_3$), 4.12 quntet (2H, $POCH_2$, J_{PH} 7.5, J_{PH} 7.5), 4.52 d and 4.72 d (1H, PCH, J_{PH} 5.0), 6.00–6.25 m (1H, POCH); δ_P 15.1, 14.9

Table. (Contd.)

Comp. no.	R^1	R^2	R^3	δ, ppm (*J*, Hz)
XXc	MeO	$CH(OMe)_2$	$OCH(Cl)CHMe_2$	δ_H: 1.00–1.17 m (6H, $CH\underline{CH_3}$), 2.10–2.30 m (1H, $\underline{CH}Me_2$), 3.41–3.62 m (1H, $\underline{CH}OCH_3$), 3.88 d (3H, $POCH_3$, J_{PH} 11.0), 4.70 d.d (1H, PCH, J_{PH} 7.2, J_{HH} 6.2), 5.98–6.18 m (1H, CHCl); δ_C: 16.29, 16.61, 36.51 d (J_{PC} 5.1), 36.32 d (J_{PC} 6.7), 52.95 d (J_{PC} 7.2), 53.06 d (J_{PC} 7.2), 92.19 d (J_{PC} 7.5), 92.65 d (J_{PC} 9.3), 99.90 d (J_{PC} 211.9), 100.90 d (J_{PC} 206.6); δ_P 15.2, 14.7
XXd	$MeCH_2O$	$CH(OCH_2Me)_2$	$OCH(Cl)CCl_3$	δ_H: 0.6–1.1 m (9H, $OCH_2\underline{CH_3}$), 3.3 q (4H, $O\underline{CH_2}CH_3$, J_{HH} 7.5), 3.85 quntet (2H, $POCH_2$, J_{PH} 7.5, J_{PH} 7.5), 4.35 d (1H, PCH, J_{PH} 7.5), 6.01 d (1H, POCH, J_{PH} 8.3); δ_P 16.2, 15.7

its initial decomposition to pyrocatechol chlorophosphite **Ib** and isobutyric aldehyde **IIb** and the subsequent interaction with P(III) chloride **Ib** of acetaldehyde **IIa** activated with triethyl phosphite.

Reaction of intermediates **IVh–IVk** with acetals was studied by an example of acetaldehyde diethyl acetal **VIII**. While mixing any of compounds **IVh–IVk** with small excess of acetal an insignificant heat evolution was observed. After two days the distillation of reaction mixture in a vacuum gave compound **IX** in a high yield. Its constants were close to those published in [15]. In the ^{1}H NMR spectrum of volatile products collected in the trap cooled by liquid nitrogen mainly the signals corresponding to the protons of corresponding aldehyde were observed.

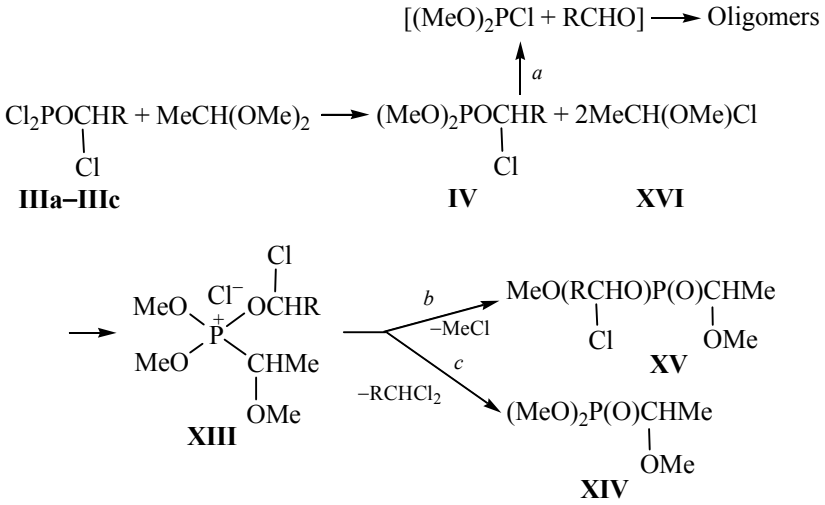
Reaction of intermediates **IVh–IVk** with triethyl orthoformate **X** also proceeded with an insignificant heat evolution. After four days in ^{31}P NMR spectrum of the reaction mixture an intense signal at δ_P 135 ppm corresponding to phosphorus atom in (pyrocatechol) ethyl phosphite was observed. Small signals appeared at δ_P 135 ppm (starting intermediate) and 46 ppm (diethyl oxymethylphosphonate **XII**). Compounds **XI** and **XII** were isolated in a pure state by distillation of reaction mixture in a vacuum, and their constants were close to that described in the literature [16].

Note that the reactions of pure pyrocatechol chlorophosphite with ethylene oxide, acetal, trialkyl orthoformate, aldehydes, activated trialkyl phosphites proceed with a significant heat evolution. In contrast, the reactions of intermediates **IVh–IVk** with these nucleophiles proceed with a small *exo*-effect, therefore we assume that the limiting stage of these reactions is the decomposition of compounds **IVh–IVk** to pyrocatechol chlorophosphite and aldehyde.

Intermediates **IIIa–IIIf** unlike compounds **IVh–IVk** have active chlorine atoms at P(III), therefore we expected that their reactions with acetals and orthoesters would proceeds with much stronger *exo*-effect. Most convenient for the investigation proved to be compounds **IIIa–IIIc**. On the other side, in the chlorine substitution stages at P(III) with alkoxy groups labile intermediates **IV** should be formed. Under the conditions of the reaction they may partially decompose to dialkyl chlorophosphite **Ic** and aldehyde (pathway *a*) and give rise to the oligomeric products [17]. With the purpose of diminishing the contribution of this pathway the reaction was carried out under cooling, and intermediate **III** was added to the excess of acetal or orthoester.

We have found that at dropwise addition of compounds **IIIa–IIIc** to acetal **VIII** under cooling a vigorous reaction took place. Vacuum distillation of the reaction mixture gave two fractions and a still. The latter was not studied specially. Nevertheless, considering that in the reactions of usual dialkyl chlorophosphites, for example, diethyl chlorophosphite, with acetals practically no still is formed, it may be suggested that its formation is provided by further reactions of decomposition products of intermediates **IVd** and **IVl, IVm** (pathway *a*). Repeated distillation of fractions permitted to isolate pure products **XIV** and **XV**.

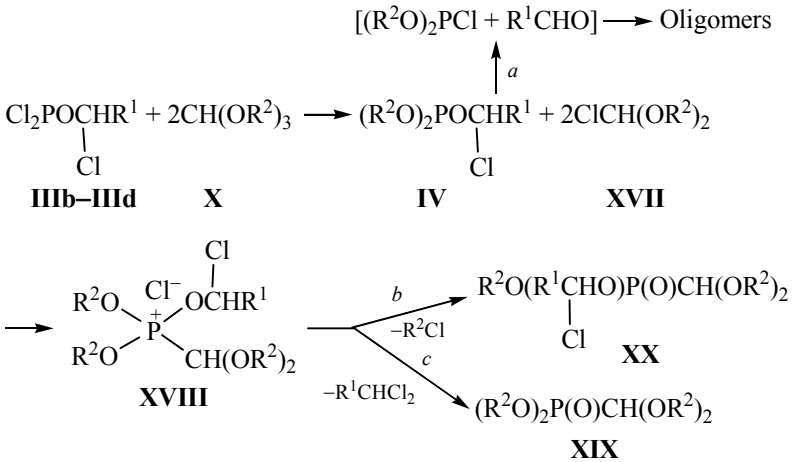
All intermediates **IIIa–IIIc** give the same low boiling compound, dimethyl 1-methoxyethylphosphonate **XIV**. The structure of the higher boiling product was found to all 1-chloroalkoxyphosphonate **XV**. Characteristics of ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **XV** are listed in the table.



IV, R = *i*-Pr (**e**), Me (**l**), Pr (**m**); **XV**, R = Me (**a**), Pr (**b**), *i*-Pr (**c**).

The formation of two products **XIV** and **XV** in this reaction can be explained by stabilization of intermediate quasiphosphonium salt **XII** via two pathways *b* and *c*, i.e., with the elimination of methyl chloride (pathway *b*) and alkylidene chloride (pathway *c*).

We have found also that at the dropwise addition of intermediates **IIIb–IIId** to orthoformate **X** an exothermal reaction proceeds. The distillation of the reaction mixture from the Arbuzov flask gave two fractions. The still was significantly smaller than in the case of the reaction of compounds **IIIb, IIIc** with acetals. Evidently due to the higher electrophilic reactivity of chloroformals **XVII** as compared to a-chloroethers **XVI** the summary contribution of the pathways *b*, *c* increases as compared to the contribution of the pathway *a*. In ^{31}P NMR spectrum of the first fraction three signals at δ_P 15.1, 14.9 (intensity ratio 2 : 1) and 16.4 ppm were observed. The ratio of summary intensity of first two signals and the intensity of the third signal is 1 : 1. By means of slow distillation from the flask equipped with the 15 cm Vigreux column pure compound **XIX** was isolated. In its ^{31}P NMR spectrum phosphorus atom gives a signal at δ_P 16.4 ppm.

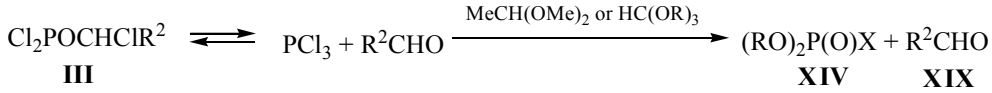


IV, R^1 = Pr, R^2 = Et (**n**); R^1 = *i*-Pr, R^2 = Me (**e**); R^1 = CCl_3, R^2 = Et (**o**); **X**, R = Me (**a**), Et (**b**); **XIX**, R^2 = Me (**a**), Et (**b**); **XX**, R^1 = Pr, R^2 = Et (**b**), R^1 = *i*-Pr, R^2 = Me (**c**); R^1 = CCl_3, R^2 = Et (**d**).

The distillation of the second fraction with the Vigreux column gave pure product **XX**. In its ^{31}P NMR spectrum two very close signals at δ_P 15.1 and 14.9 ppm with the intensity ratio 2 : 1 are found. Characteristics of ^{1}H and ^{13}C NMR spectra of compounds **XIX** and **XX** are presented in the table.

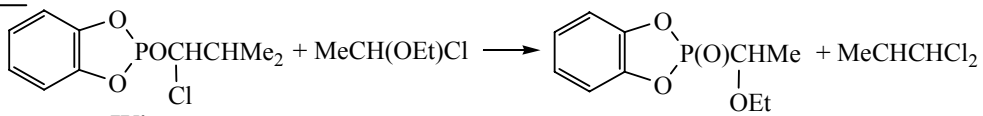
The formation of two products **XIX** and **XX** in this reaction can be ascribed evidently to the stabilization of intermediate quasiphosphonium salt **XVIII** along two pathways, , i.e., the elimination of alkyl chloride (pathway *b*) and alkylidene chloride (pathway *c*).

There exists also one more pathway leading to the formation of compounds **XIV** and **XIX**. Intermediates **III** decompose to give phosphorus trichloride **Ia** and aldehyde, and the reaction of chloride **Ia** with acetals and orthocarboxylates yields the above-mentioned compounds.

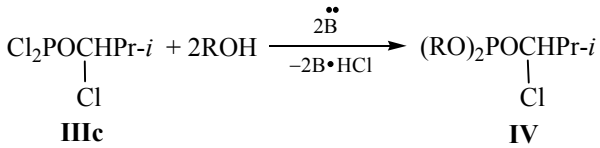


X = MeCH(OMe) (**XIV**), CH(OR)$_2$ (**XIX**).

Nevertheless, if this pathway really exists, its contribution is evidently insignificant, and these compounds are formed mainly as the result of direct interaction of intermediates **III** with acetals and orthoesters. Firstly, compounds **III** are much more stable, than intermediates **IV**. They can be stored neat in the sealed ampules. Secondly, they have active chlorine atoms on P(III), and similarly to the other P(III) chlorides react with acetals and orthoesters with strong heat liberation. Unlike that intermediates **IV** react with nucleophiles quite reluctantly. And finally, among the volatile products collected in a trap cooled with liquid nitrogen alkylidenedichloride is found. Principal possibility of its formation in the course of elimination of 1,1-dichloroalkyl group during the stabilization of intermediate quasiphosphonium salt was shown by the reaction of intermediate **IVi** with α-chloroether.



Compound **IX** prepared by this reaction and that obtained by the interaction of intermediate **IVi** with acetal have very close constants and NMR spectral characteristics. Principal possibility of the formation of compounds **IVe, IVf** which are intermediates in the reactions of orthoesters and acetals with intermediate **IIIc** was shown by their preparation by the reaction of the latter with alcohols in presence of a base.



R = Me (**e**), Et (**f**).

Compounds **IVd–IVe** are stable only in strongly diluted ether solution at 0–5°C. In ^{31}P NMR spectrum of these substances only one signal at δ_P 140 ppm is observed. It corresponds to O_3P(III) surrounding of phosphorus in trialkyl phosphites. Their structure was proved also by their oxidation to the corresponding phosphates.

Hence, it can be concluded that there exists a principal difference in the reaction of intermediates from pyrocatechol chlorophosphate **Ib** and PCl_3 with acetals and trialkyl orthoformates. The first type compounds slowly decompose to give aldehyde and chloride **Ib** which reacts with these nucleophiles. The compounds of the second type contain active chlorine atoms on P(III) and similarly to all P(III) chlorides directly react with acetals and orthoesters.

EXPERMENTAL

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

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite IVi with ethylene oxide. Etylene oxide,

5.28 g (0.088 mol) was added at +5°C to 19.73 g (0.08 mol) of compound **IVi**. The obtained mixture was kept for 6 days at +5°C, and volatile compounds were removed in a vacuum. The distillation in a high vacuum gave 13.3 g (76%) of (2-chloroethyl)pyrocatechol phosphite **V**, bp 66–68°C (0.03 mm Hg), n_D^{20} 1.5310, d_4^{20} 1.3051.

Reaction of pyrocatechol chlorophisphite with ethylene oxide. Ethylene oxide was passed slowly through 5 g (0.03 mol) of pyrocatechol chlorophosphite maintaining temperature of the reaction mixture at 10°C. After a day the reaction mixture was distilled in a vacuum to give 5.2 g (80%) of compound **V,** bp 67–69°C (0.03 mm Hg), n_D^{20} 1.5330, d_4^{20} 1.3110.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite IVi with triethyl phosphite. To a solution of 18.4 g (0.11 mol) of triethyl phosphite 23.63 g (0.096 mol) of compound **IVi** was added dropwise. After 24 h the distillation of reaction mixture in a vacuum gave 19.6 g (59%) of (2-methyl-1-diethoxyphosphorylpropyl)pyrocatechol phosphite **VIId,** bp 133–134°C (0.02 mm Hg), n_D^{20} 1.4960, d_4^{20} 1.1933 (see the table). Found, %: C 48.01; H 6.15; P 17.35. $C_{14}H_{22}O_6P$. Calculated, %: C 48.27; H 6.32; P 17.79.

Reaction of compound IVi with trimethylphosphite. Analogously to the above-described example the reaction of 10.92 g (0.044 mol) of intermediate **IVi** with 5.45 g (0.044 mol) of trimethyl phosphite yielded 7.8 g (55%) of (2-methyl-1-dimethoxyphosphorylpropyl)pyrocatechol phosphite **VIIc**, bp 135–137°C (0.1 mm Hg), n_D^{20} 1.5041, d_4^{20} 1.2135 (see the table). Found, %: P 19.85. $C_{12}H_{18}O_6P_2$. Calculated, %: P 19.35.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite IVi with trimethyl phosphite in the presence of acetaldehyde. To a mixture of 7.78 g (0.176 mol) of acetaldehyde and 6.6 g (0.053 mol) of trimethyl phosphite 10.95 g (0.044 mol) of compound **IVi** was slowly added dropwise at 10°C. After 24 h the distillation of reaction mixture in a vacuum gave 7.8 g (61%) of (1-dimethoxyphosphorylethyl)pyrocatechol phosphite **VIIa**, bp 117–118°C (0.1 mm Hg), n_D^{20} 1.5105, d_4^{20} 1.3102 (see the table).

Reaction of intermediate IVi with triethyl phosphite in the presence of 4-fold excess of acetaldehyde. Analogously to the above-presented example from 10.77 g (0.05 mol) of compound **IVi**, 8.3 g (0.05 mol) of triethyl phosphite, and 8.8 g (0.2 mol) of acetaldehyde 11.14 g (71%) of (1-diethoxyphosphorylethyl)pyrocatechol phosphite **VIIb** was obtained, bp 124–125°C (0.02 mm Hg), n_D^{20} 1.5005, d_4^{20} 1.2425 (see the table). Found, %: P 19.46. $C_{12}H_{18}O_6P_2$. Calculated, %: P 19.35.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphate IVi with 1,1-diethoxyethane. Compound **IVi**, 19.73 g (0.08 mol), was added at room temperature to 14.18 g (0.12 mol) of 1,1-diethoxyethane. An insignificant *exo*-effect was observed. After 2 days the distillation in a high vacuum gave 15.49 g (71%) of pyrocatechol 1-ethoxyethylphosphonate, bp 111°C (0.02 mm Hg), n_D^{20} 1.5060, d_4^{20} 1.2141 (see the table). Found, %: C 52.41; H 5.58; P 13.47. $C_{10}H_{13}O_4P$. Calculated, %: C 52.63; H 5.70, P 13.60.

Reaction of 2-methyl-1-chloropropyl dichlorophosphite IIIc with 1,1-dimethoxyethane. Compound **IIIc**, 9.06 g (0.043 mol), was added dropwise at 20°C to 7.8 g (0.086 mol) of 1,1-dimethoxyethane. A significant *exo*-effect was observed. The distillation of the reaction mixture in a vacuum gave 1.0 g of dimethyl 1-methoxyethylphosphonate **XIV,** bp 85°C (9 mm Hg), and 3.56 g (34%) of methyl(2-methyl-1-chloropropyl) 1-methoxyethylphosphonate **XVc**, bp 70–72°C (0.04 mm Hg), n_D^{20} 1.4419, d_4^{20} 1.1493 (see the table). Found, %: C 42.80, H 7.91; Cl 14.83; P 13.01. $C_8H_{18}ClO_4P$. Calculated, %: C 42.72; H 8.02; Cl 14.51; P 12.70.

Reaction of 1-chloroethyl dichlorophosphite IIIa with 1,1-dimethoxyethane. Analogously to the above-presented procedure from 9.6 g (0.106 mol) of 1,1-dimethoxyethane and 9.6 g (0.053 mol) of intermediate **IIIa** 0.45 g of the product **XIV**, bp 85°C (9 mm Hg) and 2.16 g (22%) of methyl(1-chloroethyl) 1-methoxyethylphosphonate **XVa** were obtained, bp 51–52°C (0.04 mm Hg), n_D^{20} 1.4371, d_4^{20} 1.1940 (see the table). Found, %: C 33.10; H 6.26; Cl 16.22; P 14.20. $C_6H_{14}ClO_4P$. Calculated, %: C 33.26; H 6.47; Cl 16.39; P 14.31.

Reaction of 1-chlorobutyl dichlorophosphite IIIb with 1,1-dimethoxyethane. Analogously to the above-presented procedure from 4.33 g (0.048 mol) of 1,1-dimethoxyethane and 5 g (0.024 mol) of intermediate **IIIb** 0.9 g of the product **XIV**, bp 85°C (9 mm Hg) [^{1}H NMR spectrum, δ, ppm: 1.5 d.d (3H, CHMe, J_{PH} 18 Hz, J_{HH} 7 Hz), 3.2 s (3H, OMe), 3.5 d (3H, POMe, J_{PH} 10 Hz), 4.5 m (1H, CH)], and 1.81 g (34%) of methyl-(1-chlorobutyl) 1-mehoxyethylphosphonate **XVb**, bp 68–71°C (0.03 mm Hg) were obtained (see the table). Found, %: C 39.01; H 7.15; Cl 14.31; P 12.35. $C_8H_{18}ClO_4P$. Calculated, %: C 39.26; H 7.36; Cl 14.51; P 12.66.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol phosphite IVi with triethyl orthoformate. Intermediate **IVi**, 21.8 g (0.088 mol), was added dropwise at room temperature to 13.1 g (0.088 mol) of triethyl orthoformate. After keeping for 96 h the vacuum distillation of the reaction mixture gave 6.7 g of pyrocatechol(ethyl) phosphite **XI**, bp 92°C (10 mm Hg), d_4^{20} 1.1925 {bp 97°C (14 mm Hg), d_4^{20} 1.1954 [16]},[^{1}H NMR spectrum, δ, ppm: 1.1 t (3H, Me, $^3J_{HH}$ 7 Hz), 3.6 quintet (2H, CH_2, $J_{HH} = J_{PH} = 7$ Hz), 6.7 m (4H, C_6H_4); ^{31}P NMR spectrum, δ_P, ppm: 128 ppm] and 5.85 g (28.8%) of pyrocatechol (diethoxymethyl)-phosphonate **XII**, bp 123–125°C (0.01 mm Hg) (see the table). Found, %: C 51.034; H 5.76; P 11.97, $C_{11}H_{15}O_5P$. Calculated, %: C 51.16,H 5.81, P 12.01.

Reaction of 2-methyl-1-chloropropyl dichlorophosphite IIIc with trimethyl orthoformate. Compound **IIIc**, 6.15 g (0.031 mol), was added dropwise to 7.16 g (0.067 mol) of trimethyl orthoformate under cooling with cold water. The mixture obtained was stirred for 0.5 h at room temperature, volatile substances were removed, and the residue was distilled in a high vacuum. Two fractions with bp 47–95°C (0.01 mm Hg) and 95–99°C (0.01 mm Hg) were obtained. The repeated distillation of these fractions with a Vigreux column gave 0.8 g of dimethyl (dimetoxymethyl)phosphonate **XIXa**, bp 47–49°C (0.01 mm Hg), and 5.3 (66%) of methyl(2-methyl-1-chloropropyl) (dimethoxymethyl)phosphonate **XXc**, bp 93–94°C (0.01 mm Hg) (see the table). Found, %: C 36.71; H 6.96; Cl 13.23; P 12.01. $C_8H_{18}ClO_3P$. Calculated, %: C 36.85; H 6.91; Cl 13.62; P 11.88.

Reaction of 1-chlorobutyl dichlorophosphite IIIb with triethyl orthoformate. Analogously to the above-presented procedure from 16 g (0.108 mol) of orthoformate and 11.33 g (0.05 mol) of intermediate **IIIb** 1.1 g of diethyl (diethoxymethyl)phosphonate **XIXb**, bp 65–66°C (0.01 mm Hg), d_4^{20} 1.0531 {127-128°C (12 mm Hg), d_4^{20} 1.0538 [9]} and 8.2 g (50%) of (1-chlorobutyl)ethyl (diethoxymethyl)phosphonate **XXb** were obtained, bp 103–104°C (0.01 mm Hg), d_4^{20} 1.078 (see the table). Found, %: C 43.01; H 7.83; Cl 12.10; P 9.89. $C_{11}H_{24}ClO_5P$. Calculated, %: C 43.64; H 7.93; Cl 11.71; P 10.23.

Reaction of 1,2,2,2-tetrachloroethyl dichlorophosphite IIId with triethyl orthoformate. Compound **IIIg**, 29.3 g (0.103 mol), was slowly added dropwise to 38.16 g (0.25 mol) of triethyl orthoformate maintaining the temperature at 20°C. Volatile compounds were removed in a vacuum. The fraction of volatile products, 8.4 g, was isolated by means of molecular distillation at the spiral temperature 100°C and residual pressure 0.03 mm Hg. ^{31}P NMR spectrum of this fraction contained two singlets at δ_P 14 and –6 ppm. First signal corresponds evidently to phosphorus atom of dietyl diethoxymethylphosphonate, but this fraction was not thoroughly studied. On the basis of elemental analysis and NMR spectra the still (16.2 g, n_D^{20} 1.1813) was characterized as 1,2,2,2-tetrachloroethyl)ethyl (diethoxymethyl)phosphonate **XXd** (see the table). Found, %: P 8.65, 8.55; Cl 38.03. Calculated, %: P 8.91; Cl 37.51.

Reaction of (2-methyl-1-chloropropyl)pyrocatechol chlorophosphite IVi with α-chloroethyl ether. α-Chloroethyl ether, 15.1 g (0.139 mol), was added dropwise under intense stirring to 34.4 g (0.139 mol) of compound **IVi**. By distillation in a vacuum 21.57 g (68%) of pyrocatechol 1-ethoxyethylphosphonate **IX** was obtained, bp 113–114°C (0.01 mm Hg), d_4^{20} 1.2150, n_D^{20} 1.5068 (see the table).

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