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Chlorinations of Derivatives of 2,2,2-Trichlorobenzo-1,3,2-dioxaphospholes

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Abstract—By ^{31}P, ^{13}C, ^{13}C-{^{1}H}, and ^{1}H NMR spectroscopy the chlorination of 4- and 5-methyl-2,2,2-trichlorobenzo-1,3,2-dioxaphosphols was shown to provide in quantitative yield 4-methyl-2,2,2,5-tetrachloro- and 6-methyl-2,2,2,5-tetrachlorobenzo-1,3,2-dioxaphosphols. Their hydrolysis led to the formation of difficultly available 4-methyl-5-chloro- and 3-methyl-4-chloro-1,2-dihydroxybenzenes. The structure of the latter compound was established by XRD analysis. The 5-methyl-2-chlorobenzo-1,3,2-dioxaphosphol treated with excess chlorine was converted in succession into 5-methyl-2,3,4,5,6,6-hexachlorocyclohex-1-en-3-yl dichlorophosphate and 5-methyl-1,2,4,4,5,6-hexachlorocyclohex-1-en-3-yl dichlorophosphate. The hydrolysis resulted in 5-methyl-2,3,4,5,6,6-hexachlorocyclohex-2-en-1-yl dihydrophosphate. The configuration of three chiral carbon atoms in the latter was established by XRD study. In the course of the chlorination the aromaticity of the *ortho*-phenylene fragment was distorted and 3,3-sigmatropic shift of the dichlorophosphoryl group occurred. The reaction with chlorine of 5-*tert*-butyl-2,2,2-trichlorobenzo-1,3,2-dioxaphosphol and 2,2,2-trichloro-benzo-1,3,2-dioxaphosphol was not selective: The reaction product obtained in excess chlorine transformed on hydrolysis into tetrachloropyrocatechol. Its solvates with water and dioxane were studies by XRD analysis.

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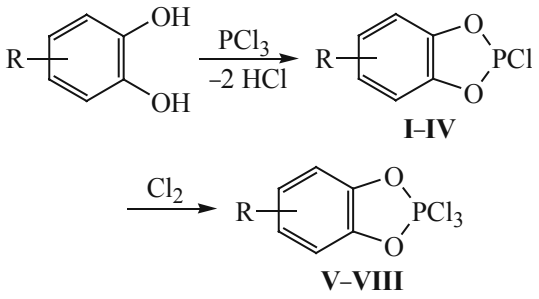
1,2-Dihydroxybenzenes (catechols or pyrocatechols) and their derivatives play an important part in organic sysnthesis and in the synthesis of natural substances and also in the metabolism of aromatic hydrocarbons [1–7]. Despite the enormous number of publications concerning their preparation the problem of selective introduction of functional groups, in particular, of halogen, into the catechol molecule remains urgent [8–10]. The electrophilic substitution with chlorine and bromine in the 2-methoxy-4-methylphenol is known to proceed nonselectively, and in the halogen excess form the corresponding 2,5,6-trihaloderivatives [11, 12]. Mono- and dihaloderivatives of some pyrocatechols were later obtained in moderate yields using milder halogenating agents ($SOCl_2$, SO_2Cl_2, CH_3COCl etc.) in various solvents [13]. The application of cyclic ethers based on pyrocatechol, like benzo[*d*]-1,3-dioxolane, proved to be efficient [14–17]. At the use of methyl-substituted anilines and phenols alongside the common substitution a rare process occurred of a distortion of the benzene ring aromaticity, and already in the conventional conditions mixtures of diastereomers of polychlorinated cyclohexen-3-ones were obtained [18]. The distortion of aromaticity was also observed at benzene chlorination under UV irradiation to provide cyclohexane and cyclohexene derivatives [19–22] and at phenol chlorination in alkaline medium [23]. No examples are known of clean and selective halogenation of cyclic systems with the catechol moiety included into a P-heterocycle (benzo-1,3,2-dioxaphosphol) (a review on the chemical properties of these compounds, see [24]).

In this study aiming at the preparation of chlorocatechols we brought into the chlorination reaction 2-chlorobenzo-λ^3-1,3,2-dioxaphosphols **I–IV**. The reaction with chlorine of these compounds occured in several stages but in all events at equimolar reagents ratio according to reports cited in [24] first formed pentacoordinate phosphorus derivatives, 2,2,2-trichlorobenzo-λ^5-1,3,2-dioxaphospholes **V–VIII** that could be isolated in high yield and purified by vacuum distillation.

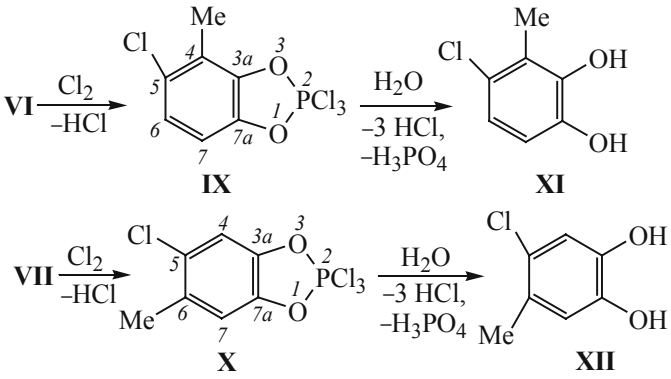


I–IV

V–VIII

R = H (**I, V**), 4-Me (**II, VI**), 5-Me (**III, VII**), 5-Bu-*t* (**IV, VIII**).

We revealed for the first time that phosphols **VI** and **VII** were capable to undergo regioselective chlorination into the benzene ring leading to the formation of compounds **IX** and **X** in high yields. In their $^{31}P-\{^1H\}$ NMR spectra characteristic signals appeared at δ_P –22.8 and –24.1 ppm.



IX **XI**

X **XII**

The introduction of a chlorine atom into the benzene ring is proved by ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum of compounds **IX** and **X** in the downfield region a spectral pattern is observed characteristic of 1,2,3,4- and 1,2,4,5-tetrasubstituted benzenes. In the $^{13}C-\{^1H\}$NMR spectra of substances **IX** and **X** four signals of carbon atoms appear in the downfield region which have no direct coupling with protons, and of two carbon atoms whose signals are split in doublets at recording the ^{13}C NMR spectra. For phosphol **IX** the resonance of atom C^7 in the spectrum $^{13}C-\{^1H\}$ is observed as a doublet with the coupling constant $^3J_{POCC^7}$ 17.4 Hz. The nuclei of *ipso*-atoms C^{3a} and C^{7a} are also easily distinguished not only due to the considerable difference in the summary effect of chlorine and methyl (stronger deshielding of C^{3a} atom), but by the multiplicity of signals in the ^{13}C NMR spectrum (a doublet of doublets for C^{7a} and a multiplet for C^{3a}). The same difference in the deshielding *para*- and *ortho*-effects of chlorine and methyl made it possible to unambiguously assign the signals of $C^{4,7}$ and $C^{3a,7a}$ in phosphol **X**. In the latter case the assignment was additionally supported by the multiplicity of signals from C^7 and C^{7a} in the ^{13}C NMR spectrum due to the couplings with the protons of methyl group.

The regiochemistry of chlorination is consistent with the electrophilic character of the reaction and can be ascribed to the joint orientation from two *ortho-para* directing substituents (methyl group and one of the oxygen atoms). In the ordinary reactions of electrophilic chlorination of aromatic compounds iron or aluminum chlorides are as a rule used as catalysts, but the halogenation of phenols or dihydroxy benzenes does not require catalysts. The easily proceeding chlorination of benzo-1,3,2-dioxaphosphol that has not been formerly known [24] is an uncommon event and it is evidently due to the catalytic effect of the pentacoordinate phosphorus atom acting as a Lewis acid on the polarization of the chlorine molecule.

The chlorination of benzophosphols **V** and **VII** with equimolar quantity of chlorine followed by hydrolysis of compounds **IX** and **X** can be regarded as a convenient selective synthesis of methyl-substituted 4- and 5-chloropyrocatechols **XI** and **XII**.

The structure of 3-methyl-4-chloropyrocatechol (**XI**) was proved by XRD analysis. Four independent molecules (*a*, *b*, *c*, *d*) differing from each other in the experimental error limits are present in the unit cell (Fig. 1). The bond distances C–C, C–Cl, and C–O are within the standard limits of this type bonds (Table 1). Only in one molecule the C–Cl bond is somewhat shortened [1.579(8) Å] because of the partial occupancy

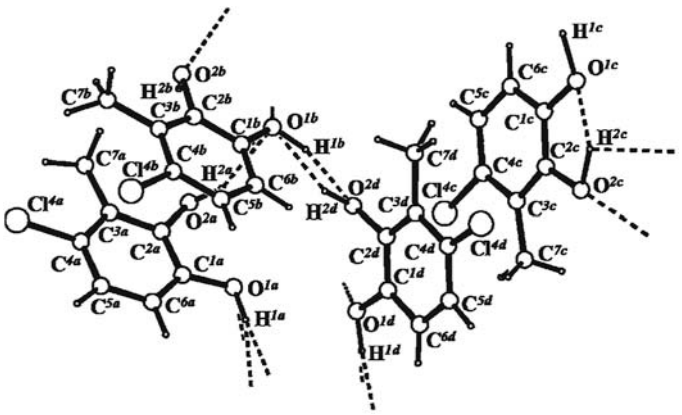


Fig. 1. Four independent molecules (*a*–*d*) of 3-methyl-4-chloropyrocatechol (**XI**) in the crystal.

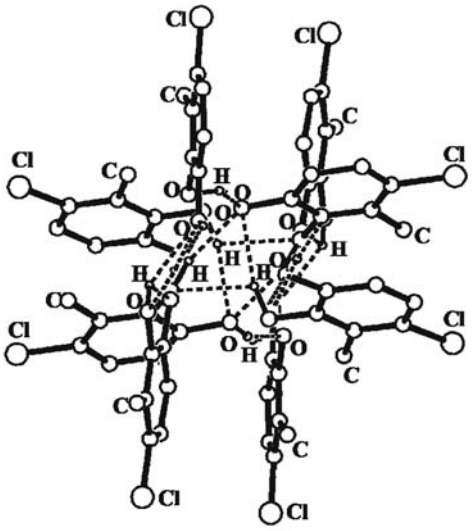


Fig. 2. The formation of supramolecular cylindrical aggregates of molecules **XI** with classic hydrogen bonds O–H···O, along 0*x* axis (only hydrogens involved in bonds formation are shown).

(50%) of this position of the chlorine atom. Benzene rings of all molecules are flat within 0.01 Å; the substituents are a little deviated from the plane of the rings in the opposite directions (alternation of substituents in the 1,2,3,4-tetrasubstituted benzene). The exocyclic angeles at the methyl group in the four independent molecyles of the substituted pyrocatechol are within the limits of an ideal value for an sp^2-hybridized carbon atom. The bond angles $Cl^4C^4C^5$ at the chlorine atom in molecules **XIa**, **XIb, XId** are slightly diminished, and in molecule **XIc** this angle is within the standard limits.

In the crystal of compound **XI** form numerous classic and nonclassical hydrogen bonds O–H···O and C–H···Cl (Table 2) that result in appearance of a spiral structure of infinite chain of molecules bound by the hydrogen bonds along 0*x* axis (Fig. 2). These spiral structures penetrate into each other by their coils. Therewith the chlorine atoms are outside of these spiral structures forming "chlorine channels." Owing to the classic hydrogen bonds O–H···O supramolecular cylindrical

Table 1. Main geometrical parameters of compound **XI** (four independent molecules): bond distances *d* (Å), bond φ and torsion τ angles (deg)

Angle	φ	Angle	φ	Angle	φ
$O^{1c}C^{1c}C^{2c}$	121.3(6)	$O^{1a}C^{1a}C^{6a}$	126.5(8)	$Cl^{4c}C^{4c}C^{3c}$	115.6(6)
$O^{1c}C^{1c}C^{6c}$	120.2(7)	$C^{2a}C^{1a}C^{6a}$	119.4(8)	$Cl^{4c}C^{4c}C^{5c}$	120.9(5)
$C^{2c}C^{1c}C^{6c}$	118.4(7)	$O^{2d}C^{2d}C^{1d}$	116.7(6)	$C^{3c}C^{4c}C^{5c}$	123.5(7)
$O^{1b}C^{1b}C^{2b}$	115.3(6)	$O^{2d}C^{2d}C^{3d}$	121.0(7)	$Cl^{4d}C^{4d}C^{3d}$	122.7(7)
$O^{1b}C^{1b}C^{6b}$	124.3(7)	$C^{1d}C^{2d}C^{3d}$	122.2(7)	$Cl^{4d}C^{4d}C^{5d}$	117.3(6)
$C^{2b}C^{1b}C^{6b}$	120.4(7)	$Cl^{4a}C^{4a}C^{5a}$	116.1(6)	$C^{3d}C^{4d}C^{5d}$	119.9(7)
$O^{1d}C^{1d}C^{2d}$	118.7(6)	$C^{3a}C^{4a}C^{5a}$	123.5(7)	$C^{4b}C^{5b}C^{6b}$	118.4(7)
$O^{1d}C^{1d}C^{6d}$	119.9(7)	$Cl^{4b}C^{4b}C^{3b}$	120.3(6)	$C^{4c}C^{5c}C^{6c}$	121.2(7)
$C^{2d}C^{1d}C^{6d}$	121.5(7)	$Cl^{4b}C^{4b}C^{5b}$	117.2(6)	$C^{4a}C^{5a}C^{6a}$	117.3(8)
$O^{1a}C^{1a}C^{2a}$	114.1(8)	$C^{3b}C^{4b}C^{5b}$	122.5(7)	$O^{2c}C^{2c}C^{1c}$	115.9(7)
Bond	*d*	Bond	*d*	Bond	*d*
Cl^{4a}–C^{4a}	1.741(8)	O^{1a}–H^{1a}	0.994(6)	C^{1c}–C^{6c}	1.38(1)
Cl^{4b}–C^{4b}	1.738(7)	O^{2b}–C^{2b}	1.363(9)	C^{1b}–C^{2b}	1.37(1)
Cl^{4c}–C^{4c}	1.741(8)	O^{2b}–H^{2b}	0.983(5)	C^{5c}–C^{6c}	1.40(1)
Cl^{4d}–C^{4d}	1.579(8)	O^{2c}–C^{2c}	1.402(8)	C^{5d}–C^{6d}	1.36(1)
O^{1c}–C^{1c}	1.384(9)	O^{2c}–H^{2c}	1.164(6)	C^{1b}–C^{6b}	1.35(1)
O^{1b}–C^{1b}	1.383(8)	O^{2a}–C^{2a}	1.381(9)	C^{1d}–C^{2d}	1.34(1)
O^{1b}–H^{1b}	0.982(5)	O^{2a}–H^{2a}	0.981(5)	C^{1d}–C^{6d}	1.40(1)
O^{1d}–C^{1d}	1.386(8)	O^{2d}–C^{2d}	1.396(8)	C^{1a}–C^{2a}	1.35(1)
O^{1d}–H^{1d}	0.993(6)	O^{2d}–H^{2d}	1.017(5)	C^{1a}–C^{6a}	1.40(1)
O^{1a}–C^{1a}	1.37(1)	C^{1c}–C^{2c}	1.37(1)	C^{2d}–C^{3d}	1.34(1)
Angle	τ	Angle	τ	Angle	τ
$H^{1b}O^{1b}C^{1b}C^{2b}$	179.6(6)	$H^{1d}O^{1d}C^{1d}C^{2d}$	179.5(6)	$H^{1a}O^{1a}C^{1a}C^{2a}$	–179.6(6)
$H^{2b}O^{2b}C^{2b}C^{1b}$	61.0(8)	$H^{2c}O^{2c}C^{2c}C^{1c}$	9.2(7)	$H^{2a}O^{2a}C^{2a}C^{1a}$	–61(1)
				$H^{2d}O^{2d}C^{2d}C^{1d}$	115.2(6)

Table 2. Parameters of hydrogen bonds in the crystal of compound **XI**

D–H···A	D–H, Å	H···A, Å	D···A, Å	Angle, deg	Symmetry operation
O^{1a}–H^{1a}···O^{1d}	0.99	2.33	2.811(8)	109	$-x, -1/2 + y, 1/2 - z$
O^{1a}–H^{1a}···O^{2c}	0.99	2.07	3.056(8)	172	$-1 + x, 1/2 - y, -1/2 + z$
O^{1b}–H^{1b}···O^{2d}	0.98	1.95	2.881(7)	157	–
O^{1c}–H^{1c}···O^{2b}	1.26	1.46	2.688(8)	161	–
O^{1d}–H^{1d}···O^{1a}	0.99	1.89	2.811(8)	153	$-x, 1/2 + y, 1/2 - z$
O^{2a}–H^{2a}···O^{2b}	0.98	2.56	3.054(7)	111	$1 - x, -1/2 + y, 1/2 - z$
O^{2a}–H^{2a}···O^{1b}	0.98	2.41	3.320(7)	154	$x, 1/2 - y, -1/2 + z$
O^{2b}–H^{2b}···O^{1b}	0.98	2.08	2.942(6)	145	$1 - x, 1 - y, 1 - z$
O^{2c}–H^{2c}···O^{1c}	1.16	1.83	2.699(8)	127	–
O^{2c}–H^{2c}···O^{1d}	1.16	2.31	2.824(7)	104	$1 - x, 1 - y, 1 - z$
O^{2d}–H^{2d}···O^{1b}	1.02	2.04	2.881(7)	138	–
C^{7c}–H^{71c}···Cl^{4c}	1.23	2.34	3.039(8)	113	–
C^{7b}–H^{72b}···O^{2b}	0.97	2.44	2.809(8)	103	–
C^{7d}–H^{72d}···Cl^{4d}	1.00	2.57	3.04(1)	108	–
C^{7a}–H^{73a}···Cl^{4a}	1.00	2.52	3.052(8)	113	–

aggregates arise; one such aggregate is shown in Fig. 2 (view along 0*x* axis, only hydrogens involved in bonds formation are shown).

Compound **XII** was formerly obtained by more complex method [25], and also isolated as a metabolism product of some microorganisms [26, 27]. Its dichlorodioxolane derivative also was known [17]. Catechol XI was not previously synthesized but it was described as a metabolism product of 3-chloro-2-methylaniline in bacteria *Phodococeus prodochrous* [25] and also as a metabolism product of 2-chlorotoluene [20, 28, 29].

Dioxaphosphol **X** is capable of further reaction with chlorine under mild conditions with the distortion of the aromaticity of the benzo fragment. We succeeded to monitor the process by ^{31}P NMR spectroscopy and demonstrated that the stages are sufficiently different in kinetics; the latter made it possible to establish the structure of some intermediate compounds by means ^{13}C NMR spectroscopy. In the first stage as shown by the peak with the chemical shift δ_P –31.5 ppm formed a compound with a pentacoordinate phosphorus **XIII**. The distortion of the aromaticity of the benzene ring and formation of a single diastereomer at arising of four chiral centers (C^{3a}, C^4, C^5, C^{7a}) was established based on the ^{13}C-{^{1}H} and ^{13}C NMR spectra of this compound. In molecule XIII five of the seven carbon nuclei resonate in the strong field characteristic of sp^3-hybridized carbon atoms. The presence of two signals in the region 95–101 ppm indicates the addition of chlorine across the p-bond OC^{3a}=$C^{7a}O$ resulting in formation of a fragment $OC^{3a}(Cl)C^{7a}(Cl)O$ [30]. The nuclei of the *ipso*-atoms C^{3a} and C^{7a} are distinguished thanks to the difference in the electronic effect of the chloromethylene and alkenyl substituents (stronger deshielding of C^{3a} atom). The signal of another sp^3-hybridized atom (C^4) appeared in ^{13}C-{^{1}H} as a doublet with a characteristic *trans*-constant $^3J_{PCCC}$ 18.9 Hz. In the spectrum registered without decoupling from protons the latter signal additionally split into a doublet of quartets that was possible only in case a methyl was attached to C^5. The nultiplicity of the remaining signals corresponded to a double bond C^6=C^7.

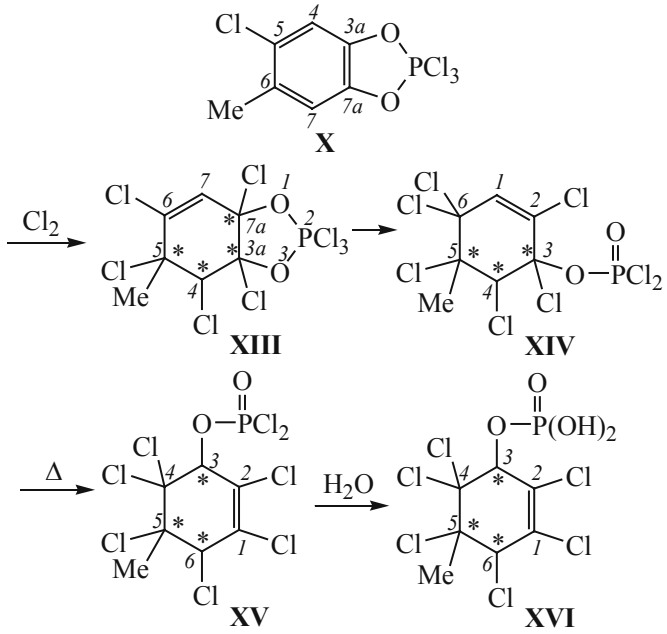
No further chlorine addition occurred to the double bond of compound **XIII**. Dioxaphosphol **XIII** at storage for 3–4 days (20°C) gradually transformed into a thick colorless oily phosphate **XIV** (δ_P –1.3 ppm) along the route of the nonclassical version of Arbuzov reaction. Its structure was established from the ^{13}C and ^{13}C–{^{1}H} NMR spectra. Unlike compound **XIII** phosphate **XIV** has in the spectrum a single peak characteristic of the moiety OC(Cl)C and belonging to C^3 (doublet, $^2J_{POC}$ 15.2 Hz). Two downfield signals corresponding to the carbon atoms at the double bond in this case appear as doublets owing to the coupling with the phosphorus nucleus. Besides the atoms C^4, C^5, and C^6 involved into coupling with the protons of methyl resonated upfield in the region characteristic of sp^3-hybridized carbon atoms. In this stage alongside the allylic rearrangement a regioselective rupture of the C^{3a}–O bond occurred with the formation of a phosphoryl group. The regiochemistry of the process presumably is governed by the stability of the intermediately arising allyl carbocation with the positive charge rather on C^{3a} and not on C^{7a} atom.

In phosphate **XIV** at long storage (20°C) or at heating an uncommon 3,3-sigmatropic shift of the dichlorophosphate group occurred formerly unknown from publications. It may be regarded as a version of Claisen 3,3-rearrangement [31]. According to NMR spectra, phosphate **XV** formed as a single diastereomer with a P–O bond stable against hydrolysis.

Compound **XVI** crystallized as a salt of alkylphosphoric acid with a DMSO molecule **XVII** and formed a solvate with a water molecule. XRD data for salt **XVII** (Fig. 3, Table 3) show the presence in the single crystal of two enantiomers *A* and *B* in the ratio 1:1 of a configuration $C^{3}{}_{R}C^{5}{}_{S}C^{6}{}_{S}/C^{3}{}_{S}C^{5}{}_{R}C^{6}{}_{R}$. The carbocycle in molecule *A* occurs in a *semichair* conformation: Four-

Table 3. Main geometrical parameters of solvate **XVII** (two independent molecules): bond distances *d* (Å), bond φ and torsion τ angles (deg)

Angle	φ	Angle	φ	Angle	φ
$O^{2A}P^{1A}O^{3A}$	112.4(5)	$C^{5A}C^{4A}Cl^{4A}$	110.1(7)	$C^{6B}C^{1B}Cl^{1B}$	113.7(7)
$O^{2A}P^{1A}O^{4A}$	115.3(5)	$C^{7A}C^{4A}Cl^{4A}$	109.4(8)	$C^{1B}C^{2B}C^{3B}$	122.4(9)
$O^{3A}P^{1A}O^{4A}$	106.9(5)	$C^{3A}C^{4A}Cl^{4A}$	103.2(7)	$C^{1B}C^{2B}Cl^{2B}$	122.1(8)
$O^{2A}P^{1A}O^{1A}$	110.2(4)	$C^{4A}C^{5A}C^{6A}$	109.8(9)	$C^{3B}C^{2B}Cl^{2B}$	115.4(8)
$O^{3A}P^{1A}O^{1A}$	104.3(5)	$C^{4A}C^{5A}Cl^{5A}$	112.8(7)	$C^{2B}C^{3B}C^{4B}$	115.4(9)
$O^{4A}P^{1A}O^{1A}$	107.2(5)	$C^{6A}C^{5A}Cl^{6A}$	106.5(6)	$C^{2B}C^{3B}Cl^{3B}$	106.0(7)
$C^{6A}O^{1A}P^{1A}$	123.7(6)	$Cl^{5A}C^{5A}Cl^{6A}$	108.3(6)	$C^{3B}C^{4B}C^{7B}$	114.9(9)
$C^{2A}C^{1A}C^{6A}$	123.1(7)	$O^{1A}C^{6A}C^{1A}$	112.0(7)	$C^{5B}C^{4B}Cl^{4B}$	105.6(7)
$C^{2A}C^{1A}Cl^{1A}$	122.3(8)	$O^{1A}C^{6A}C^{5A}$	108.1(8)	$C^{7B}C^{4B}Cl^{4B}$	106.6(8)
$C^{6A}C^{1A}Cl^{1A}$	114.4(7)	$C^{1A}C^{6A}C^{5A}$	112.6(8)	$C^{4B}C^{5B}C^{6B}$	111.9(8)
$C^{1A}C^{2A}C^{3A}$	124.7(8)	$O^{2B}P^{1B}O^{3B}$	117.3(5)	$C^{6B}C^{5B}Cl^{5B}$	107.6(8)
$C^{1A}C^{2A}Cl^{2A}$	123.0(7)	$O^{2B}P^{1B}O^{4B}$	111.1(5)	$C^{4B}C^{5B}Cl^{6B}$	107.9(8)
$C^{3A}C^{2A}Cl^{2A}$	112.2(7)	$O^{3B}P^{1B}O^{4B}$	108.8(5)	$C^{6B}C^{5B}Cl^{6B}$	109.1(7)
$C^{2A}C^{3A}C^{4A}$	111.2(8)	$O^{2B}P^{1B}O^{1B}$	108.5(4)	$O^{1B}C^{6B}C^{1B}$	112.2(8)
$C^{2A}C^{3A}Cl^{3A}$	110.3(7)	$O^{4B}P^{1B}O^{1B}$	103.6(5)	$O^{1B}C^{6B}C^{5B}$	107.9(8)
$C^{5A}C^{4A}C^{7A}$	111.3(9)	$C^{6B}O^{1B}P^{1B}$	124.6(7)	$C^{1B}C^{6B}C^{5B}$	110.2(9)
Bond	*d*	Bond	*d*	Bond	*d*
Cl^{1A}–C^{1A}	1.685(9)	C^{1A}–C^{2A}	1.31(1)	Cl^{2B}–C^{2B}	1.70(1)
Cl^{2A}–C^{2A}	1.705(9)	C^{1A}–C^{6A}	1.53(2)	Cl^{3B}–C^{3B}	1.87(1)
Cl^{4A}–C^{4A}	1.800(9)	C^{2A}–C^{3A}	1.52(1)	Cl^{6B}–C^{5B}	1.78(1)
P^{1A}–O^{2A}	1.498(8)	C^{3A}–C^{4A}	1.60(2)	Cl^{4B}–C^{4B}	1.84(1)
P^{1A}–O^{3A}	1.511(9)	C^{4A}–C^{5A}	1.52(2)	P^{1B}–O^{2B}	1.490(8)
P^{1A}–O^{4A}	1.512(8)	C^{4A}–C^{7A}	1.59(2)	P^{1B}–O^{3B}	1.497(8)
P^{1A}–O^{1A}	1.571(8)	C^{5A}–C^{6A}	1.58(1)	P^{1B}–O^{4B}	1.559(9)
C^{1A}–C^{6A}	1.45(1)	Cl^{1B}–C^{1B}	1.719(9)	P^{1B}–O^{1B}	1.588(8)
Angle	τ	Angle	τ	Angle	τ
$Cl^{1A}C^{1A}C^{6A}O^{1A}$	42(1)	$Cl^{3A}C^{3A}C^{4A}Cl^{4A}$	158.6(6)	$C^{1B}C^{2B}C^{3B}C^{4B}$	5(2)
$C^{2A}C^{1A}C^{6A}C^{5A}$	–22(1)	$Cl^{3A}C^{3A}C^{4A}C^{7A}$	42(1)	$Cl^{2B}C^{2B}C^{3B}Cl^{3B}$	66.2(9)
$Cl^{1A}C^{1A}C^{6A}C^{5A}$	163.6(7)	$C^{3A}C^{4A}C^{5A}C^{6A}$	–58(1)	$C^{1B}C^{2B}C^{3B}Cl^{3B}$	–118(1)
$C^{2A}C^{1A}C^{6A}O^{1A}$	–144(1)	$C^{7A}C^{4A}C^{5A}Cl^{5A}$	–61(1)	$C^{2B}C^{3B}C^{4B}C^{5B}$	–30(1)
$Cl^{2A}C^{2A}C^{3A}Cl^{3A}$	–70.1(9)	$C^{7A}C^{4A}C^{5A}Cl^{6A}$	61(1)	$C^{7B}C^{4B}C^{5B}Cl^{5B}$	–53(1)
$Cl^{2A}C^{2A}C^{3A}C^{4A}$	161.7(7)	$Cl^{6A}C^{5A}C^{6A}O^{1A}$	–69.3(9)	$Cl^{4B}C^{4B}C^{5B}Cl^{5B}$	63.1(8)
$C^{1A}C^{2A}C^{3A}Cl^{3A}$	111(1)	$Cl^{5A}C^{5A}C^{6A}O^{1A}$	47.1(9)	$Cl^{6B}C^{5B}C^{6B}O^{1B}$	–50.2(9)
$C^{1A}C^{2A}C^{3A}C^{4A}$	–17(2)	$C^{4A}C^{5A}C^{6A}C^{1A}$	47(1)	$Cl^{5B}C^{5B}C^{6B}O^{1B}$	66.7(9)
$Cl^{3A}C^{3A}C^{4A}C^{5A}$	–82.9(9)	$C^{2B}C^{1B}C^{6B}C^{5B}$	24(2)	$C^{4B}C^{5B}C^{6B}C^{1B}$	–47(1)
$C^{2A}C^{3A}C^{4A}C^{5A}$	43(1)	$Cl^{1B}C^{1B}C^{6B}O^{1B}$	–43(1)	$Cl^{6B}C^{5B}C^{6B}C^{1B}$	72.6(9)



atom fragment $C^{6}C^{1}C^{2}C^{3}$ is planar within 0.08(1) Å, atoms C^{4} and C^{5} deviate in different directions from this plane by –0.31(1) and 0.31(1) Å; in molecule *B* the carbocycle takes *semichair* conformation, nearly sofa: Four-atom fragment $C^{6}C^{1}C^{2}C^{3}$ is planar within 0.02(1) Å, atoms C^{5} and C^{4} deviate from this plane by –0.50(2) and 0.17(1) Å respectively. The deviation of these atoms in different directions just permits the nomination of this conformation as *semichair*. However the minimal deviation of atom C^{4B} [0.17(1) Å] from the plane $C^{6B}C^{1B}C^{2B}C^{3B}$ also permits to regard the five-atom fragment $C^{6B}C^{1B}C^{2B}C^{3B}C^{4B}$ as nearly planar and the cycle conformation, as *sofa*. Bond lengths C–Cl at the double bond C=C are shortened due to the effect of the phosphorus substituent at atom C^{1} [Cl^{1A}–C^{1A} 1.67(1),

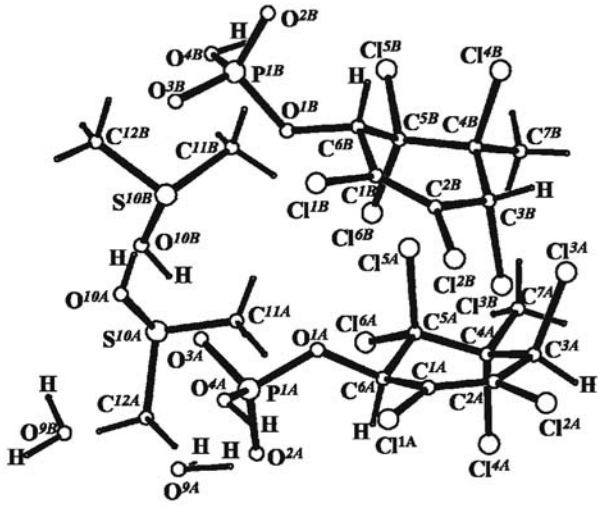


Fig. 3. Structure of phosphate salt with DMSO **XVII** (solvate with water) in the crystal.

Cl^{2A}–C^{2A} 1.68(1), Cl^{1B}–C^{1B} 1.71(1), Cl^{2B}–C^{2B} 1.65(1) Å]. Inasmuch as in the crystal lattice four solvate molecules are present (2DMSO and $2H_2O$) numerous classic hydrogen bonds O–H···O form in the crystal that result in infinite layers along one of the crystallographic axes. The system of hydrogen bonds in molecule **XVII** is shown in Fig. 4. The intra- and intermolecular hydrogen bonds O–H···O and O–H···Cl lead to the formation of a bilayer structure alond the 0*y* axis. Parameters of the bonds are given in Table 4.

Unlike 5-methyl-2,2,2,6-tetrachlorobenzo[*d*]-1,3,2-dioxaphosphol (**X**), 4-methyl-2,2,2,5-tetra-chlorobenzo-[*d*]-1,3,2-dioxaphosphol (**IX**) did not react with excess chlorine under the common conditions. 5-*tert*-Butyl-2,2,2-trichlorobenzo[*d*]-1,3,2-dioxaphosphol (**VIII**) and unsubstituted compound **I** underwent a nonselective chlorination, and at the equimolar reagents ratio formed

Table 4. Parameters of hydrogen bonds in the crystal of salt **XVII** (solvate with water)

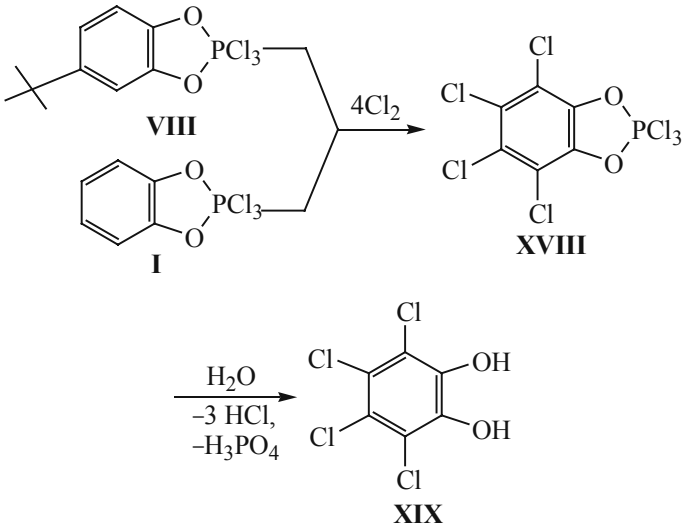
D–H···A	D–H, Å	H···A, Å	D···A, Å	Angle, deg	Symmetry operation
O^{4A}–H^{4A}···Cl^{1A}	0.82	2.70	3.344(9)	136	–
O^{4A}–H^{4A}···O^{2B}	0.82	1.94	2.56(1)	132	–
O^{4B}–H^{4B}···O^{2A}	0.82	2.06	2.65(1)	128	–
O^{10A}–H^{10A}···O^{9B}	0.82	1.92	2.49(2)	126	1 – *x*, 1 – *y*, 1 – *z*
O^{10B}–H^{10B}···O^{3A}	0.82	1.65	2.40(2)	151	–
O^{9A}–H^{91A}···Cl^{1B}	0.96(3)	2.77(5)	3.53(1)	136(6)	–1 + *x*, *y*, *z*
O^{9A}–H^{91A}···O^{2A}	0.96(3)	2.13(7)	2.74(1)	120(5)	–
O^{9B}–H^{91B}···S^{10A}	1.0(2)	2.8(2)	3.43(1)	121(18)	1 – *x*, 1 – *y*, 1 – *z*
O^{9B}–H^{91B}···O^{10A}	1.0(2)	1.7(3)	2.49(2)	136.00	1 – *x*, 1 – *y*, 1 – *z*
O^{9A}–H^{92A}···O^{3B}	0.96(9)	1.86(8)	2.70(1)	144(10)	–1 + *x*, *y*, *z*
O^{9B}–H^{92B}···O^{3B}	0.96(6)	1.98(17)	2.48(2)	110(13)	1 – *x*, –*y*, 1 – *z*

Table 5. Geometric parameters of tetrachloropyrocatechol solvate with dioxane **XIX**: bond distances *d* (Å) and bond angles φ (deg)

Angle	φ	Angle	φ	Angle	φ	Angle	φ
$C^1O^1H^1$	101(2)	$O^2C^2C^1$	115.2(2)	$C^2C^3C^4$	120.2(2)	$Cl^5C^5C^6$	119.5(2)
$C^2O^2H^2$	113(2)	$O^2C^2C^3$	124.8(2)	$Cl^4C^4C^3$	119.8(1)	$C^4C^5C^6$	120.2(2)
$O^1C^1C^2$	120.4(2)	$C^1C^2C^3$	120.0(2)	$Cl^4C^4C^5$	120.5(2)	$Cl^6C^6C^1$	119.3(2)
$O^1C^1C^6$	119.5(2)	$Cl^3C^3C^2$	119.0(1)	$C^3C^4C^5$	119.7(2)	$Cl^6C^6C^5$	120.9(2)
$C^2C^1C^6$	120.2(2)	$Cl^3C^3C^4$	120.8(1)	$Cl^5C^5C^4$	120.3(1)	$C^1C^6C^5$	119.8(2)
Bond	*d*	Bond	*d*	Bond	*d*	Bond	*d*
Cl^3–C^3	1.723(2)	O^1–C^1	1.358(2)	O^{11}–C^{12}	1.417(4)	C^3–C^4	1.398(3)
Cl^4–C^4	1.722(2)	O^1–H^1	0.73(3)	C^1–C^2	1.390(3)	C^4–C^5	1.379(3)
Cl^5–C^5	1.726(2)	O^2–C^2	1.358(2)	C^1–C^6	1.383(3)	C^5–C^6	1.403(3)
Cl^6–C^6	1.714(2)	O^2–H^2	0.76(3)	C^2–C^3	1.385(3)	C^{10}–C^{12}	1.479(4)

a complex mixture of chlorinated benzophosphols. The prolonged passing of chlorine in a large excess through solutions of phosphol **VIII** in dichloromethane resulted in the formation of 2,2,2,4,5,6,7-heptachlorobenzo[*d*]-λ⁵-1,3,2-dioxaphosphol (**XVIII**). In the course of the process the *tert*-butyl group suffered an *ipso*-replacement, and the arising *tert*-butyl chloride was identified in the ^{1}H NMR spectrum. In the ^{31}P NMR spectrum phosphol **XVIII** gave rise to an upfield singlet at δ –22.9 ppm.

By hydrolysis of compound **XVIII** we obtained tetrachloropyrocatechol **XIX** whose structure was established by XRD analysis of two types of single crystals obtained: solvate with dioxane *a* and solvate with water *b*. The general view of solvates with dioxane *a*



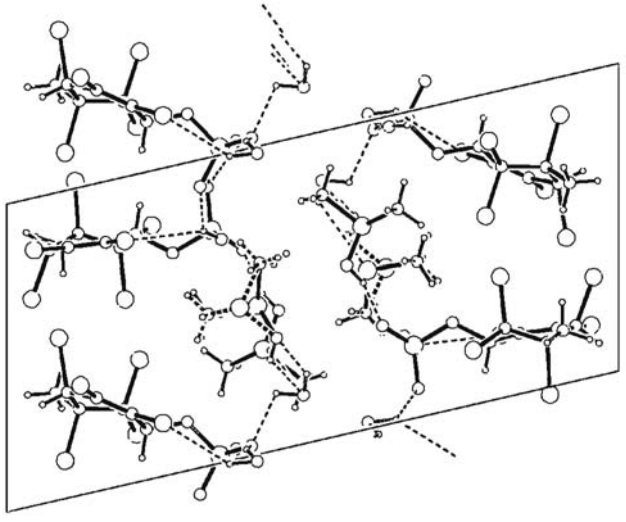


Fig. 4. Hydrogen bonds system in the crystal of salt **XVII** (view along 0°C axis).

and with water *b* are presented on Figs. 5 and 6 respectively. The parameters of cataechol **XIX** (bond distances and bond angles) are compiled in Table 5.

In the crystal of solvate *a* with dioxane of tetrachloropyrocatechol **XIX** an intramolecular and intermolecular hydrogen bonds exist. The bifurcate intramolecular hydrogen bond O^1–$H^1\cdots O^2$ has the following parameters: O^1–H^1 0.73(3), $H^1\cdots O^2$ 2.15(3), $O^1\cdots O^2$ 2.655(2) Å, angle O^1–$H^1\cdots O^2$ 127(2)°. Another hydrogen bond is of three-center character and is involved into an intra-molecular contact O^2–$H^2\cdots Cl^3$ [O^2–H^2 0.76(3), 2.72(3), $O^2\cdots Cl^3$ 3.020(1) Å, angle 106(2)°] and anintermolecular contact O^2–$H^2\cdots O^{11}$ with parameters: O^2–H^2 0.76(3), $H^2\cdots O^{11}$ 1.92(3), $O^2\cdots O^{11}$ 2.630(2) Å, angle O^2–$H^2\cdots O^{11}$ 156(3)°.

In the crystal of solvate *b* of tetrachloropyrocatechol with water (Fig. 6) a complex three-dimensional network

formed because of intermolecular hydrogen bonds O–H···O and O–H···Cl (Fig. 7). Tetrachloropyrocatechol formed crystalline adducts with triphenylphosphine oxide [32], triphenylphosphine oxide and water [32], triphenylarsine oxide [33], and 2,2-bis(diisopropylamino)-5-[bis(diisopropylamino)phosphinyl]-6,7,8,9-tetrachloro-1,3,4,2-λ^5-benzoxazaphosphepine and dichloromethane [34] where also various types of intra- and intermolecular hydrogen bonds were present.

Thus it was shown for the first time that the transformation of an *ortho*-hydroxy fragment into a cyclic phosphol resulted in an increased regio- and stereoselectivity of chlorination of substituted benzenes. This procedure can be a convenient method for chlorocatechols preparation.

EXPERIMENTAL

The solvents and reagents used were purified and dried by conventional methods. All reactions were carried out under an atmosphere of dry argon. NMR spectra were registered on spectrometers Bruker MSL-400 [400 (^{1}H), 162.0 (^{31}P), 100.6 MHz (^{13}C)], Bruker WM-250 [250 MHz (^{1}H)], Bruker CXP-100 [36.48 MHz (^{31}P)]. The δ_P values were measured relative to an external reference (H_3PO_4), δ_C and δ_H values, with respect to internal reference (HMDS). Parameters of X-ray diffraction experiments are compiled in Table 6.

4-Methyl-2-chlorobenzo-1,3,2-dioxaphosphol (II). A mixture of 12.8 g of methylpyrocatechol, 14 ml of PCl_3, and several drops of water was stirred for 1.5 h at 100°C. Excess PCl_3 was removed in a vacuum (12 mm Hg), the residue was distilled. Yield 17.3 g (89%), bp 65°C (1 mm Hg), n_D^{20} 1.5630. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s (3H, CH_3), 6.99–7.10 m (3H, H^{5-7}, *ABC*). ^{31}P-{^{1}H} NMR spectrum (36.46 MHz, $CDCl_3$): δ_P 174.2 ppm.

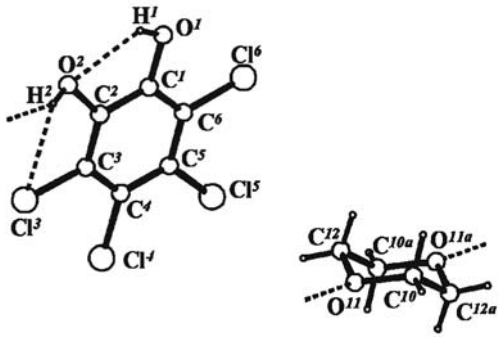


Fig. 5. Molecule of tetrachloropyrocatechol **XIX** solvate *a* with dioxane in the crystal (hydrogen bonds are shown by dotted lines).

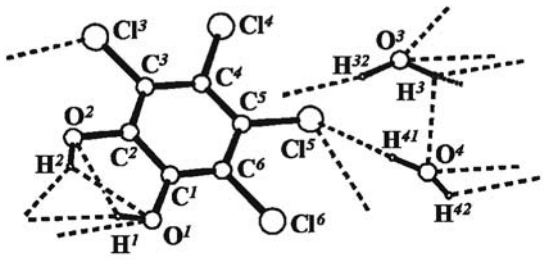


Fig. 6. Molecule of tetrachloropyrocatechol **XIX** solvate *b* with water in the crystal (hydrogen bonds are shown by dotted lines).

5-Methyl-2-chlorobenzo-1,3,2-dioxaphosphol (III). A mixture of 10 g of 4-methylpyrocatechol, 22.2 ml of PCl_3, and several drops of water was stirred for 1 h at 100–110°C, then it was maintained in a vacuum to remove excess PCl_3. The residue was distilled. Yield 13.7 g (91%), bp 65°C (1 mm Hg). ^{31}P-{^{1}H} NMR spectrum: δ_P 176.6 ppm

4-Methyl-2,2,2-trichlorobenzo-1,3,2-dioxaphosphol (VI). To a solution of 3.85 g of dioxaphosphol **II** in 15 ml of dichloromethane was added at stirring under an argon atmosphere while cooling (–70°C) a solution

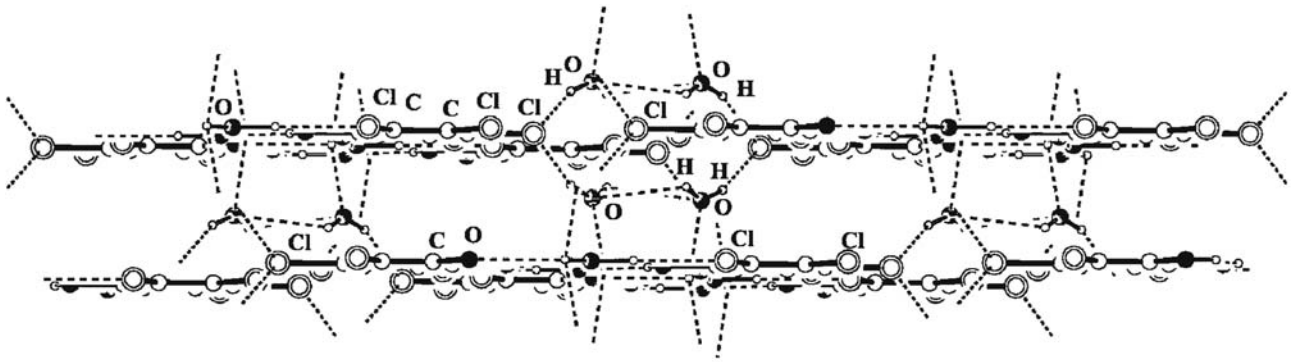


Fig. 7. Hydrogen bonds system in the crystal of tetrachloropyrocatechol **XIX** solvate with water.

Table 6. Crystal parameters of compounds **XI, XVII**, and **XIX**, and the conditions of XRD experiments[a]

Parameter	**XI**[b]	**XVII**[c]	**XIX** (solvate *b*)[c]	**XIX** (solvate *a*)[b]
Color, habitus	Transparent, prismatic			Transparent, needle-like
Empirical formula	$C_7H_7O_2Cl$	$C_7H_6O_4Cl_6P{\cdot}C_2H_7OS{\cdot}H_2O$	$C_6H_2O_2Cl_4{\cdot}3H_2O$	$C_6H_2O_2Cl_4{\cdot}1/2C_4H_8O_2$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P 21/c	P –1	C 2/m	P –1
Unit cell parameters[d]	*a* 13.152(2) Å *b* 14.347(3) Å *c* 15.364(2) Å β 100.82(2)?	*a* 8.756(8) Å *b* 10.472(8) Å *c* 21.64(2) Å α 102.04(7)° β 99.18(7) ° γ 94.24(7) °	*a* 18.087(4) Å *b* 6.797(1) Å *c* 9.537(2) Å β 109.17(3) °	*a* 7.046(2) Å *b* 8.287(2) Å *c* 9.893(3) Å α 83.15(3) ° β 70.35(2) ° γ 84.97(2) °
Volume, A°3	2847.6(8)	1904(3)	1107.4(4)	539.5(3)
Z	4	2	4	2
M	634.34	989.88	301.92	291.95
D_{calc}, g/cm^3	1.480	1.727	1.811	1.797
μ, cm^{-1}	4.637	102.8	10.65	10.832
F(000)	1312	1000	608	292
Radiation (λ, A°)	MoK_α (λ 0.71073)	CuK_α (λ 1.54184)	MoK_α (λ 0.71073)	
Range of θ	$4.3 \le \theta \le 57.3$	$2.12 \le \theta \le 27.4$	$2.12 \le \theta \le 27.4$	$2.12 \le \theta \le 27.4$
Range of indices measurement	$-13 \le h \le 12$, $-14 \le k \le 0$, $-14 \le l \le 15$	$-9 \le h \le 9$, $-11 \le k \le 11$, $-23 \le l \le 0$	$0 \le h \le 19$, $0 \le k \le 7$, $-10 \le l \le 9$	$-8 \le h \le 8$, $-10 \le k \le 10$, $-12 \le l \le 0$
Measured reflexions	5873	8110	799	2323
Observed reflexions with $I > 3\sigma(I)$	1825	2484	227	1881
Accounting for extinction	Not performed[e]			
Conditions of revealing and refining of hydrogen atoms	Revealed from the difference series, their contibution into structural amplitudes was accounted for with fixed position and temperature factors in the final refinement stage			Revealed from the difference series, refined isotropically
Final values of *R* and R_w	0.062, 0.066	0.096, 0.222	0.060, 0.109	0.035, 0.047
Fitting parameter Δ/σ	2.290/0.00	1.066/0.008	0.907/0.00	1.673/0.00
Number of independent reflexions and refined parameters	1825/361	4620/471	771/84	1881/160

[a] Diffractometer Enraf-Nonius CAD-4; scanning ω/2θ; variable scanning rate, 1–16.4 deg/min by θ; no correction of intensity of control reflexions was done; applied programs of XRD analysis MolEN, AlphaStation 200 [35]. [b]Structure solved by the direct method, program SIR [36]; refinement by full-matrix least-squares method. The intermolecular contacts, in particular, hydrogen bonds, in the crystals were analyzed with the use of PLATON software [37]. [c]Structure solved by the direct method, program SIR [36]; refinement by SHELX program [38]. [d]Figures in parentheses are standard deviations. [e]The extiction was not taken into account because of weakly reflecting crystal.

of 1.45 g of chlorine in 10 ml of dichloromethane. The reaction mixture was maintained in a vacuum to remove excess chlorine and solvent. Yield 97%. Thick yellowish oily substance, bp 97–101°C (0.8 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s (CH_3), 7.17 br.d (H^7, $^3J_{H^6CCH^7}$ 8.8 Hz), 6.99–7.04 br.m (H^5, H^6, $^3J_{H^6CCH^5}$ 8.5 Hz). ^{13}C NMR spectrum [here and hereinafter the form of signal indicated in parentheses corresponds to the spectrum ^{13}C-{^{1}H}] ($CDCl_3$), δ, ppm: 140.10 m (d) [C^{3a}, ^2J(POC^{3a}) 1.3 Hz], 121.28 d.d.q.d (d) [C^4, ^3J(POCC^4) 17.0, ^3J(HCCC^4) 6.7–6.8, ^3J(HC^{6}CC^4) 7.1, ^2J(HC^{5}C^4) 2.0 Hz], 124.81 d.d.q (s) [C^5, ^1J(HC^5) 160.4, ^3J(HC^{7}CC^5) 7.6, ^3J(HCCC^5) 5.0 Hz], 122.74 d (s) [C^6, ^1J(HC^6) 163.9 Hz], 107.99 d.d.d (d) [C^7, ^1J(HC^7) 167.6, ^3J(POCC^7) 18.0, ^3J(HC^{5}CC^7) 8.8 Hz], 142.23 br.d (br.s) [C^{7a}, ^3J(HC^{6}CC^{7a}) 10.2 Hz], 14.62 br.q.d (d) [CH_3, ^1J(HC) 128.2, ^3J(POCCC) 1.1 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P –25.7 ppm.

5-Methyl-2,2,2-trichlorobenzo-1,3,2-dioxaphosphol (VII). To 7.4 g of phosphite **III** at –60°C was added a solution of 2.8 g of chlorine in 15 ml of dichloromethane, then the solvent and excess chlorine were removed. Yield 97%. Thick yellowish oily substance, bp 95–100°C (0.8 mm Hg). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 142.84 d.d.d (d) [C^{3a}, ^3J(HC^{7}CC^{3a}) 7.1, ^2J(HC^{4}C^{3a}) 3.6, ^2J(POC^{3a}) 0.8 Hz], 111.32 d.d.q.d (d) [C^4, ^3J(POCC^4) 17.6, ^3J(HC^{6}CC^4) 7.7, ^3J(HCCC^4) 5.1, ^4J(HC^{7}CCC^4) 1.4 Hz], 133.81 d.q (s) [C^5, ^3J(HC^{7}CC^5) 7.8, ^2J(HCC^5) 6.1 Hz], 123.51 d.d.q.d (C) [C^6, ^1J(HC^6) 161.4, ^3J(HC^{4}CC^6) 7.0, ^3J(HCCC^6) 5.1, ^2J(HC^{7}C^6) 1.1 Hz], 110.43 d.d (d) [C^7, ^1J(HC^7) 166.7, ^3J(POCC^7) 17.7 Hz], 140.40 m (d) [C^{7a}, ^2J(POC^{7a}) 0.8 Hz], 21.21 q.d.d (d) [CH_3, ^1J(HC) 127.2, ^3J(HC^{4}CC) 4.7, ^3J(HC^{6}CC) 4.7 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, C_6H_6): δ_P –27.3 ppm

4-Methyl-2,2,2,5-tetrachlorobenzo-1,3,2-dioxaphosphol (IX). To a solution of 3.6 g of dioxaphosphol **II** in 15 ml of dichloromethane was added at stirring while cooling (–60°C) a solution of excess chlorine (4 g) in 20 ml of dichloromethane. The reaction mixture was slowly warmed to 20°C and left standing for 6 days. The solvent and excess chlorine were removed in a vacuum (12 mm Hg). Yield 97%. Thick yellowish oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.32 s (CH_3), 6.87 br.d.d [H^7, ^3J(H^{6}CCH^7) 8.6, ^4J(POCCH^7) 1.0 Hz], 7.04 br.d.d [H^6, ^3J(H^{6}CCH^7) 8.6, ^5J(POCCCH^7) 1.4 Hz]. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 141.87 m (d) [C^{3a}, ^2J(POC^{3a}) 2.1 Hz], 120.27 d.d.q (d) [C^4, ^3J(POCC^4) 16.5, ^3J(HC^{6}CC^4) 6.0–6.2, ^2J(HCC^4) 6.0–6.2 Hz], 129.02 d.q.d (s) [C^5, ^3J(HC^{7}CC^5) 10.7, ^3J(HCCC^5) 5.4, ^2J(HC^{6}C^5) 4.4 Hz], 122.89 d (s) [C^6, ^1J(HC^6) 168.5 Hz], 108.77 d.d (d) [C^7, ^1J(HC^7) 170.2, ^3J(POCC^7) 17.4 Hz], 140.33 br.d.d (br.s) [C^{7a}, ^3J(HC^{6}CC^{7a}) 12.0, ^2J(HC^{7}C^{7a}) 3.6 Hz], 12.74 q.d (d) [CH_3, ^1J(HC) 129.9, ^4J(POCCC) 1.1 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P –22.8 ppm

6-Methyl-2,2,2,5-tetrachlorobenzo-1,3,2-dioxaphosphol (X). To a solution of 6.2 g of phosphite **III** in 30 ml of dichloromethane was added at stirring while cooling (–60°C) a solution of 5 g of chlorine in 25 ml of dichloromethane. The reaction mixture was slowly warmed to 20°C and left standing for 3 days. The solvent and excess chlorine were removed in a vacuum. Yield 9.3 g (96%). Thick yellowish oily substance. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 141.04 d.d.d (d) [C^{3a}, ^2J(POC^{3a}) 0.9, ^3J(HC^{7}CC^{3a}) 7.5, ^2J(HC^{4}C^{3a}) 4.3 Hz], 111.62 d.d (d) [C^4, ^1J(HC^4) 170.8, ^3J(POCC^4) 17.7, ^4J(HCCCC^4) 0.8–0.9 Hz], 131.28 q.d (s) [C^6, ^2J(HC^{4}CC^6) 12.0, ^2J(HCC^6) 6.0 Hz], 128.08 d.q.d (s) [C^5, ^3J(HC^{7}CC^5) 10.3, ^2J(HC^{4}C^5) 5.1, ^3J(HCCC^5) 5.2 Hz], 112.63 d.d.q.d (d) [C^7, ^1J(HC^7) 166.4, ^3J(POCC^7) 17.3, ^3J(HCCC^7) 5.2, ^4J(HC^{4}CCC^7) 1.3 Hz], 141.11 d.d.d.q (d) [C^{7a}, ^3J(HC^{4}CC^{7a}) 7.5, ^2J(HC^{7}C^{7a}) 4.3, ^2J(POC^{7a}) 1.6, ^4J(HCCCC^{7a}) 0.9–1.0 Hz], 20.03 q.d (s) [CH_3, ^1J(HC) 132.6, ^3J(HC^{7}CC) 3.0 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P –24.1 ppm.

3-Methyl-4-chloropyrocatechol (XI). Into a mixture of 7 ml of water and 1.5 ml of HCl was carefully added dropwise at stirring (20°C) 5.4 g of phosphol **IX**. A strong heat evolution and hydrogen chloride liberation was observed. The reaction product was extracted with hexane at boiling. From the separated hexane layer in some time crystals precipitated. The crystals were filtered off and dried in a vacuum (12 mm Hg). Yield 1.1 g (38%), mp 53–54°C. IR spectrum, ν, cm^{-1}: 454, 544, 584, 655, 727, 817, 839, 854, 893, 1003, 1034, 1113, 1143, 1185, 1209, 1295, 1377, 1461, 1509, 1603, 2855, 2925, 3299. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.19 s (3H, CH_3), 6.656–6.70 m (2H, H^5, H^6, *AB*, ^3J 8.6 Hz), 8.54 br.s and 9.37 br.s (2H, OH). Found, %: C 53.11; H 4.77. $C_7H_7ClO_2$. Calculated, %: C 53.0; H 4.42.

4-Methyl-5-chloropyrocatechol (XII). To a solution of 10.0 ml of water and 0.5 ml of hydrochloric acid was added at vigorous stirring (20°C) 9.3 g of phosphorane **X**. The reaction mixture was heated at stirring on a water bath (60°C) for 1 h. The crystals precipitated on cooling were filtered off and recrystallized from hexane. Yield 2.3 g (46%), mp 106–107°C. IR spectrum, ν, cm^{-1}: 453, 544, 586, 656, 726, 817, 837, 857, 892, 943, 1002, 1035,

1113, 1143, 1185, 1209, 1292, 1350, 1377, 1462, 1511, 1603,1658, 1721, 1932, 2855, 2925, 2955 3298. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.16 s (3H, CH_3), 6.71 s and 6.77 s (2H, H^4, H^6). Found, %: C 53.17; H 4.59. Calculated, %: C 53.0; H 4.42.

Chlorination of dioxaphosphol (X). To a solution of 6.5 g of phosphol **X** in 20 ml of CH_2Cl_2 while stiring under an argon atmosphere was added a solution of 1.9 g of chlorine in 20 ml of CH_2Cl_2 at –50°C. After 3 days a mixture was obtained of compounds **XIII** (δ_P –23.2 ppm) and **XIV** (δ_P –1.3 ppm) in a ratio 3:2; after 6 days the ratio reached 1:6. Compound **XIII** completely converted in phosphate **XIV** within two weeks (25°C).

5-Methyl-2,2,2,3a,4,5,6,7a-octachloro-3a,7a,4,5-tetrahydrobenzo-1,3,2-dioxaphosphol (XIII). Yellowish oily substance. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 95.35 d.d.d (d) [C^{7a}, ^3J(HC^{4}CC^{7a}) 2.3, ^2J(POC^{7a}) 1.2, ^2J(HC^{7}C^{7a}) 1.0–1.1 Hz], 122.94 d.d (s) [C^7, ^1J(HC^7) 177.5, ^4J(HC^{4}CCC^7) 1.4 Hz], 139.22 d.q (s) [C^6, ^2J(HC^{7}C^6) 5.4, ^3J(HC^{8}CC^6) 4.3 Hz], 69.95 m (s) (C^5), 69.12 d.d.q (d) [C^4, ^1J(HC^4) 156.1, ^3J(POCC^4) 18.9, ^3J(HC^{8}CC^4) 3.5 Hz], 100.77 d.d.d (d) [C^{3a}, ^2J(POC^{3a}) 5.9, ^3J(HC^{7}CC^{3a}) 5.9, ^2J(HC^{4}C^{3a}) 2.5 Hz], 25.38 d.q (s) [C^8H_3, ^1J(HC^8) 132.7, ^3J(HC^{4}CC^8) 3.1 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P –31.5 ppm.

5-Methyl-2,3,4,5,6,6-hexachlorocyclohex-1-en-3-yl dichlorophosphate (XIV). Colorless oily substance. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 132.30 d.d (d) [C^1, ^1J(HC^1) 180.4, ^4J(POCCC^1) 1.4 Hz], 130.13 d.d (d) [C^2, ^2J(HC^{4}C^2) 5.1, ^3J(POCC^2) 3.0 Hz], 96.91 d.d.d (d) [C^3, ^2J(POC^3) 15.2, ^3J(HC^{4}CC^3) 11.3, ^2J(HCC^3) 1.2 Hz], 71.16 d.d.q (d) [C^4, ^1J(HC^4) 158.5, ^3J(POCC^4) 3.5, ^2J(HCC^4) 3.3 Hz], 75.37 d.d.q (s) [C^5, ^3J(HC^{4}CC^5) 5.3, ^2J(HCC^5) 5.3, ^2J(HCC^5) 4.2 Hz], 87.97 m (s) [C^6, ^3J(HC^{7}CC^6) 4.2, ^3J(HCCC^6) 2.7, ^2J(HCC^6) 1.5 Hz], 23.00 d.d (s) [C^7, ^1J(HC^7) 132.7, ^3J(HC^{4}CC^7) 4.4 Hz]. ^{31}P-{^{1}H} NMR spectrum (162.0 MHz, $CDCl_3$): δ_P –1.3 ppm.

5-Methyl-1,2,4,4,5,6-hexachlorocyclohex-1-en-3-yl dichlorophosphate (XV) was obtained by heating (180°C, 5 min) of phosphate **XIV**. Yellow transparent viscous fluid containing 90% of compound **XV** (3.5 g), bp 145–148°C (1 mm Hg). ^{1}H NMR spectrum (400 MHz, $CDCl_3$), δ, ppm: 5.94 br.d (1H, H^3, $^3J_{POCH}$ 12.0 Hz), 5.03 br.s (1H, H^6), 2.13 br.s (3H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 126.62 br.s (br.s) (C^1), 132.00 br.s (br.s) (C^2), 84.26 d.d (d) [C^3, ^1J(HC^3) 162.3, ^2J(POC^3) 7.8 Hz], 89.83 br.m (d) [C^4, ^3J(POCC^4) 2.5 Hz], 73.95 br.s (s) (C^5), 65.39 br.d (br.s) [C^6, ^1J(HC^6) 163.4 Hz], 25.63 br.q (br.s) [C^7H_3, ^1J(HC^7) 132.8 Hz]. ^{31}P NMR spectrum (162.0 MHz, $CDCl_3$), δ, ppm: 13.2 d ($^3J_{POCH}$ 12.0 Hz).

5-Methyl-2,3,4,5,6,6- hexachlorocyclohex-1-en-3-yl dihydrophosphate (XVI) was obtained by hydrolysis of phosphate **XV** in aqueous acetone. After prolonged crystallization from aqueous DMSO colorless crystals of phosphate **XVI** were obtained as solvate **XVII** with DMSO and water, mp 211°C. ^{1}H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 2.08 br.s (3H, CH_3), 5.60 d (1H, H^6, $^3J_{POCH}$ 12.6 Hz), 5.69 d (1H, H^3, $^6J_{POCCCCH}$ 1.1 Hz). Found, %: C 21.63; H 3.32; P 6.19. $C_7H_6Cl_6O_4P\cdot C_2H_7OS\cdot H_2O$. Calculated, %: C 21.82; H 3.03; P 6.26.

Chlorination of 2,2,2-trichlorobenzo-1,3,2-dioxaphosphol (V). Through a solution of 4.1 g of compound **V** in 10 ml of CH_2Cl_2 at –60°C was passed excess chlorine. Dichloromethane was distilled off in a vacuum, to the residue 10 ml of H_2O and 1.5 ml of HCl was added, and the mixture was boiled for 2.5 h. The water and organic layers separated. From the water layer precipitated crystals of solvate *b* of tetrachloropyrocatechol **XIX** with water, mp 183°C. Crystals for XRD analysis were obtained by recrystallization of compound **XIX** from water and dioxane [solvate *a* with dioxane, mp 176–179°C (decomp.)].

Chlorination of 5-*tert*-butyl-2,2,2-trichlorobenzo-1,3,2-dioxaphosphol (VIII). Through a solution of 8.5 g of compound **VIII** in 20 ml of CH_2Cl_2 at –40°C was passed excess chlorine. The solvent was removed in a vacuum, to the residue 15 ml of H_2O and 5 ml of HCl was added dropwise. The reaction mixture was boiled for 2.5 h, and then dark-brown oily organic layer separated from the water layer. From the water layer gradually precipitated transparent needle crystals that were filtered off and recrystallized from water. Yield of solvate *b* of tetrachloropyrocatechol **XIX** 0.12 g, mp 183–184°C (decomp.).

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