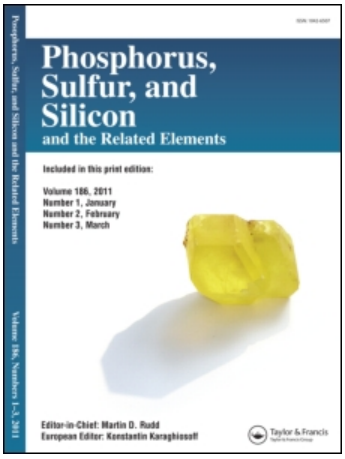

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SYNTHESIS AND CHEMISTRY OF DIALKYL-AND DIARYLTRICHLOROMETHYLPHOSPHINES

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SYNTHESIS AND CHEMISTRY OF DIALKYL- AND DIARYLTRICHLOROMETHYLPHOSPHINES

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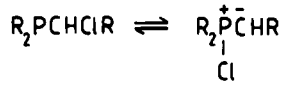
The synthesis of dialkyl- and diaryltrichloromethylphosphines and their reactions with various electrophiles and nucleophiles are reported.

Key words: Dialkyltrichloromethylphosphines; diphenyltrichloro-methylphosphine; *P*-chloro-dialkyl-dichloromethylenephosphoranes; *P*-chloro-diphenyl-dichloromethylenephosphorane; phosphonium salt; chlorination; dehydration; condensation.

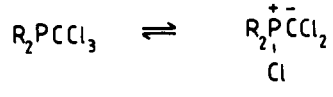
The specific tautomerism of 1-halogenoalkylphosphines, **1**, and *P*-halogenoylides, **2**, involving reversible halogenotropic shift has recently been well recognized.[1] It has been also found that the position of equilibrium **1** ⇌ **2** (Scheme 1) depends strongly on the chemical features of the substituents at the P—C diad.[1b,2] This tautomeric system proved to be very interesting from the theoretical point of view[1b] and very useful in organic synthesis.[1b,c,3] In this paper we report the new systems consisting of dialkyl- and diaryl-trichloromethylphosphines **3**, and corresponding *P*-chloroylides **4**, (Scheme 2), as well their reactions with selected nucleophiles and electrophiles.

It has been patented that α-halogenated tertiary phosphines are useful starting materials for the synthesis of organophosphorus polymers and can be easily prepared by treatment of the phosphines R_1R_2PH (R_1 and R_2 = hydrogen, hydrocarbon or fluorinated hydrocarbon groups) with the appriopriate halogenated hydrocarbons.[4] Unfortunately all our attempts following the patent procedure to obtain the dialkyltrichloromethylphosphines, **3a-d**, from the corresponding dialkylphosphines and carbon tetrachloride failed. However, the compounds **3a-d** were successfully prepared when dialkylphosphines were reacted with carbon tetrachloride in the presence of one equivalent of triethylamine in an aprotic solvent and at low temperature (Scheme 3). Although the reaction between diphenylphosphine and carbon tetrachloride occurred as described in the patent[4] the resulting diphenyltrichloromethylphosphine (**3e**) was strongly contaminated with diphenylchlorophosphine (30–45%). Purity of the phosphine **3e** was considerably improved



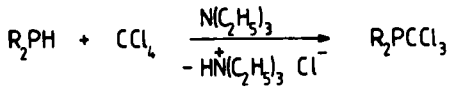
1 **2**

SCHEME 1



3 **4**

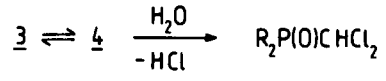
SCHEME 2



3a-e

3	a	b	c	d	e
R	C_2H_5	n-C_3H_7	n-C_4H_9	n-C_8H_{17}	C_6H_5

SCHEME 3



5a-e

5	a	b	c	d	e
R	C_2H_5	n-C_3H_7	n-C_4H_9	n-C_8H_{17}	C_6H_5

SCHEME 4

when the above reaction was performed in the presence of one equivalent of triethylamine.

Dialkyltrichloromethylphosphines, **3a-c**, are thermally unstable and cannot be purified by distillation but they can be used "in situ" for further transformations. As expected, **3a-e**, slowly decompose in a variety of inert solvents at room temperature. When the temperature is decreased to 0 ÷ 5°C the decomposition is considerably limited. The phosphines **3a-e** were characterized spectroscopically (^{31}P-NMR, ^{13}C-NMR and MS, Table I) and chemically. Analysis of the spectral data leads to the conclusion that the phosphine/ylide equilibrium is strongly shifted towards the phosphine tautomer. This is consistent with the following observations:

- each of the ^{31}P-NMR spectrum shows a single signal of similar chemical shift,
- the observed value of $^1J_{P\text{-}CCl} \simeq 70$ Hz rather corresponds to the phosphine than to the ylide tautomer, which according to the reported data should have $^1J_{P\text{-}CCl}$ value in the range above 120Hz.[3a]

The MS spectra of **3a-e** exhibited the expected fragmentation patterns including molecular ion signals. Upon treatment with water the phosphines **3a-e** are hydrolized to the corresponding dialkyldichloromethyl-phosphine oxides **5a-e** (Scheme 4).

Due to the presence of the electron withdrawing trichloromethyl group the phosphines **3a-e** are unsusceptible for oxygenation and can be used without any special precautions.

The reaction of dialkyltrichloromethylphosphines **3** with nonenolizable carbonyl compounds, inorganic acids, secondary amines, and halogens gives a spectrum of

TABLE 1

Dialkyltrichloromethylphosphines, **3a-d**, and diphenyltrichloromethylphosphine **3e**

3	*R*	Yield[a] %	Molecular[b] formula	^{31}P-NMR (C_6D_6/H_3PO_4 ext.) (ppm)	MS[c]	^{13}C-NMR (C_6D_6/TMS int)
a	C_2H_5	95	$C_5H_{10}Cl_3P$ (207.5)	58	206, 208, 210(M^+; 8, 8.3, 2.7); 150, 152, 154(100,100,30)	10.3(d, $^2J_{PC}$ = 19.1Hz, CH_3), 21.0(d, $^1J_{PC}$ = 19.1Hz, CH_2) 101.8(d, $^1J_{PC}$ = 71Hz, CCl_3).
b	*n*-C_3H_7	92	$C_7H_{14}Cl_3P$ (235.5)	53	234, 236, 238(M^+; 25.0, 25.8, 7.3) 192, 194, 196(100, 100, 30)	15.9(d, $^3J_{PC}$ = 13.2Hz, CH_3) 19.4(d, $^2J_{PC}$ = 19.1Hz, $\underline{C}H_2CH_2P$) 31.0(d, $^1J_{PC}$ = 19.2Hz, CH_2P) 101.5(d, $^1J_{PC}$ = 70.6Hz, CCl_3)
c	*n*-C_4H_9	90	$C_9H_{18}Cl_3P$ (263.6)	52	262, 264, 266(M^+; 4.6, 4.7, 1.7) 178, 180, 182(20.0, 20.0, 7.1) 78(100)	13.9(s, CH_3), 25.4(d, $^3J_{PC}$ = 13.3Hz $\underline{C}H_2CH_3$), 28.1(d, $^1J_{PC}$ = 19.1Hz, $\overline{C}H_2P$)[d], 28.6(d, $^2J_{PC}$ = 19.1Hz, $\underline{C}H_2CH_2P$),[d] 101.7(d, $^1J_{PC}$ = 72.1Hz, CCl_3)
d	*n*-C_8H_{17}	87	$C_{17}H_{34}Cl_3P$ (375.8)	52.8	374, 376, 378(M^+; 2.6, 2.4, 0.8)43(100)	101.7(d, $^1J_{PC}$ = 72.0Hz, CCl_3)
e	C_6H_5	85 ÷ 95	oil[4]	54.3	302, 304, 306(M^+; 19.7, 19.8, 6.3)185(100)	98.8(d, $^1J_{PC}$ = 76.4Hz, CCl_3)

[a] Yields were based on isolated phosphine oxide **5a-e** obtained from hydrolysis of **3a-e**.
[b] Microanalyses have not been performed.
[c] Glass-inlet system.
[d] Tentative assignment.

TABLE 2

Phosphoroorganic compounds formed in the reaction of **3a** and **3e** with electrophilic and nucleophilic substrates

Entry	Compound	Yield %	m.p.(°C) or b.p. (°C)/torr	Molecular[f] formula	IR ν(cm^{-1})	^{31}P-NMR δ(ppm)	^{1}H-NMR(TMS) δ ppm, J(Hz)
1	**7**	78[a]	90/0.2[c]	$C_{12}H_{16}Cl_3OP$ (313.5)		−2.25 (C_6D_6)	($CDCl_3$)1.3(6H, dt, $^3J_{PH}$ = 22, $^3J_{HH}$ = 7, C<u>H</u>$_3$CH$_2$P), 1.35–2.1(4H, *m*, CH$_2$P)5.5(*d*, = 2.5, C<u>H</u>(C_6H_5), 7.5–7.9(5H arom.).
2	**5e**	85[b]	205–206 (benzene)	$C_{13}H_{11}Cl_2OP$ (285.1)	1190 (P=O)	33 ($CHCl_3$)	($CDCl_3$)6.16(1H, *d*, $^3J_{PH}$ = 1.9, $CHCl_2$), 7.2 8.1(10H arom.).
3	**12a**	62[c]	144–146[d]	$C_6H_{11}Cl_4P$ (243.9)		85 (CH_2Cl_2)	(CD_2Cl_2)1.3(6H, dt, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 24, 3.25(4H, dq, $^3J_{HH}$ = 7.5, $^2J_{PH}$ = 10, CH_2), 8.8(1H, *d*, $^2J_{PH}$ = 10, $CHCl_2$).
4	**12b**	67	159–162[d]	$C_9H_{21}Cl_3NP$ (280.6)		69 (CH_2Cl_2)	(CH_2Cl_2)1.1(6H, *t*, $^3J_{HH}$ = 7, NCH$_2$C<u>H</u>$_3$), 1.3 dt, $^3J_{PH}$ = 10.5, $^3J_{HH}$ = 7, PCH$_2$C<u>H</u>$_3$), 2.8 *m*, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 12.5, NC<u>H</u>$_2$), 3.28(*m*, $^3J_{HH}$ = 7, $^2J_{PH}$ = 11, PCH$_2$), 8.18(1H, $^2J_{PH}$ = 4, $CHCl_2$).
5	**12c**	65	64–67[d]	$C_5H_{10}Cl_5P$ (278.4)		113.5 (CH_2Cl_2)	(CD_2Cl_2)1.58(6H, dt, $^3J_{HH}$ = 7, $^3J_{PH}$ = 26, 3.55(4H, dq, $^3J_{HH}$ = 7, $^2J_{HH}$ = 7, $^2J_{PH}$ = CH$_2$).
6	**13**	78	112–115/0.5	$C_5H_{11}Cl_2PS$ (205.1)	632[g] (P=S)	70 ($CDCl_3$)	($CDCl_3$)1.15(6H, dt, $^3J_{HH}$ = 7, $^3J_{PH}$ = 20, C 2.1(4H, *m*, CH$_2$), 6.15(1H, *d*, $^2J_{PH}$ = 2, C

[a] Estimated from the integrated intensities of the ^{31}P-NMR peaks of the crude product.

[b] Formed in the chlorination reaction with phosphine 3 (see Table 3, footnote b).

[c] Product partly undergoes thermal decomposition during destillation to give a cycloelimination product.

[d] Recrystallized by dissolving in hot dichloromethane and reprecipitation with an excess of ether; hydroscopic product.

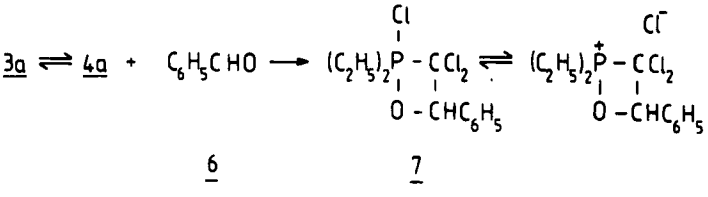
[e] Yield corresponds to the product formed in the reaction (8).

[f] Satisfactory microanalyses obtained: C ± 0.35, H ± 0.25, P ± 0.25.

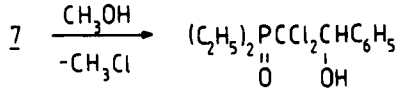
[g] Recorded using an UR-10 Spectrophotometer (C. Zeiss).

different phosphonium salts which can undergo subsequent transformations leading to a variety of products with interesting functionalities. Representative examples of these reactions are presented in Table II. The diethyltrichloromethylphosphine (**3a**) is readily added to benzaldehyde (**6**) (entry 1, Table II) producing 2,2-diethyl-4-phenyl-2,3,3-trichloro-1,2 λ^5 oxaphosphetane (**7**) (Scheme 5). The structure of the oxaphosphetane **7** was unambigously corroborated by the corresponding ^{1}H-NMR and ^{31}P-NMR spectra, as well by the results of its chemical transformations. Thus, as expected, simple methanolysis of **7** gave exclusively diethyl-(1,1-dichloro-2-hydroxy-2-phenylethyl)phosphine oxide (**10**) (Scheme 6). In turn, according to the prediction, the thermal cycloelimination of **7** afforded 2,2-dichlorostyrene (**9**) and diethyl phosphinie chloride (**8**) in very good yields (Scheme 7). It is worth to note that ^{31}P-NMR chemical shift of **7** is similar to those of known oxaphosphetanes.[3a]

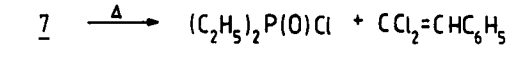
Reactions of **3** with chlorine, hydrogen chloride and diethylamine have all features of electrophilic and nucleophilic additions, respectively, and lead to the formation of new phosphonium salts **12a-c**, (Scheme 8, entry 3–5, Table II). The reaction of **3a** with hydrogen sulfide follows a different route giving rise to the formation of the chlorophosphonium salt **12a** and the phosphine sulfide **13**, (Scheme 9).



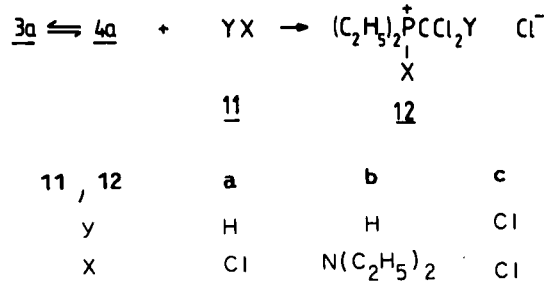
SCHEME 5



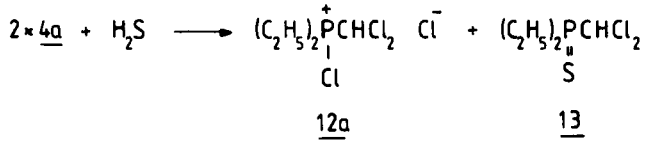
SCHEME 6



SCHEME 7



SCHEME 8



SCHEME 9

Yields, physical constans, analytical and spectroscopic data of the salts **12a-c** and phosphine sulfide **13** are presented in Table II.

The phosphines **3** can also be effectively used as a chlorinating reagents. The chlorination of alcohols and thiols with **3a** have been found to give the corresponding alkyl halides **15** in high yields (entry 1–3, Table III, Scheme 10). It is likely that the mechanism of these reactions is reminiscent of the mechanism proposed for the chlorination of alcohols and thiols with Ph_3P/CCl_4 system.[5]

The chlorination of alcohols is highly stereospecific and occurrs with inversion of configuration. Stereochemistry of the OH → Cl exchange was tested by reacting **3a** with optically active diethyl malate (entry 4, Table III). As determined by comparing the optical purity of the starting *L*(−)-diethyl malate[6,7] with that of the resulting *D*(+)-2-chlorosuccinate[8] the OH → Cl exchange proceeds with 98% inversion of configuration at the carbon atom.

The chlorination of enolizable carbonyl compounds, e.g., acetyl-acetone, with **3a** results in the formation of the corresponding β-chlorovinylketone (entry 5, Table III). The same result was obtained with the Ph_3P/CCl_4 system.[9] When diethylphosphinic acid was treated with phosphine **3a**, diethylphosphinyl chloride and tetraethyl pyrophosphinate were formed.[10] Diethyltrichloromethylphosphine (**3a**) can also be used for chlorination of benzanilide (Scheme 11) affording *N*-phenylbenzoimidoylchloride (**16**).[11] Chlorination of benzophenone oxime leads also to the formation of *N*-phenylbenzoimidoylchloride[12] (Scheme 12), however this reaction is more complex. It is very likely that **15a** constitutes the intermediate which is stabilized by the Beckmann rearrangement to produce the second intermediate **16a**. The later is a precursor of the final product **16**.

The phosphine **3a** can also be used as an effective dehydrating (entry 8, Table III) or condensing agent.[13] Acylation of phenol (entry 9, Table III) and benzylamine

TABLE 3

Dialkyl- and diaryltrichloromethylphosphines **3** as a chlorinating, dehydrating and condensing agent

Entry	Substrate(s)[a]	Product[b]	Yield[c]	m.p.(°C) or b.p.(°C)/torr
1	$C_6H_5CH_2OH$	$C_6H_5CH_2Cl$	94[f]	64/12
2	n-C_3H_7SH	n-C_3H_7Cl	88[f]	[d]
3	n-C_3H_7OH	n-C_3H_7Cl	91[f]	[d]
4	$C_2H_5OCCHCH_2COC_2H_5$ (OOH, O)	$C_2H_5OCCHCH_2COC_2H_5$[e] (OCl, O)	72	49–50/0.1, lit[g] 48–50/0.11
5	$CH_3CCH{=}CCH_3$ (O, OH)	$CH_3CCH{=}CClCH_3$ (O)	63	48/12; lit.[9] 44–50/23
6	$C_6H_5NHCC_6H_5$ (O)	$C_6H_5N{=}CClC_6H_5$	82	90/0.2[g]; lit[11] 136/1.2
7	$(C_6H_5)_2C{=}NOH$	$C_6H_5N{=}CClC_6H_5$	65	90/0.2[g]; lit[12]
8	$CH_3C(O)NH_2$	$CH_3C{\equiv}N$	64	[d]
9	CH_3COOH/C_6H_5OH	$CH_3C(O)OC_6H_5$	68	105/12
10	$CH_3COOH/C_6H_5CH_2NH_2$	$CH_3C(O)NHCH_2C_6H_5$	82	61

[a] Diethyltrichloromethylphosphine (**3a**), entry no. 1–10, and diphenyltrichloromethylphosphine (**3e**), entry 1–3, were used.

[b] The phosphoroorganic by-products: $(C_2H_5)_2P(O)CHCl_2$ (**5a**), $(C_6H_5)_2P(O)CHCl_2$ (**5e**) and $(C_2H_5)_2P(S)CHCl_2$ (**13**) were distilled (**5a**, 135–136°C/0.5 torr; **13**, 110°C/0.8 torr) or crystallized from benzene (**5e**, 205–206°C). For analytical and spectroscopic data of **5e**, **13** and **14** see Table 2.

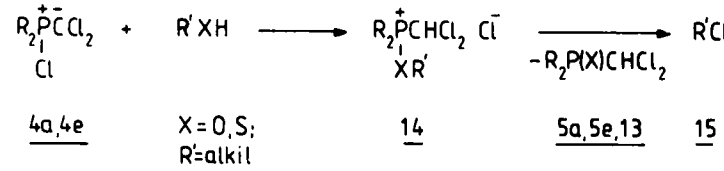
[c] Spectral properties (IR, ^{1}H-NMR) of isolated compounds have been compared with those of authentic samples.

[d] Product was distilled out from the reaction mixture with dichloromethane and its yield determined by G.L.C.

[e] D(+)-2-chlorosuccinate of α_D^{20} + 29.8° ($CHCl_3$, c 0.45), [lit.[8] α_D^{21} + 31°], was obtained starting with L-(−)-diethyl malate of α_D^{20} − 10.9 (methol, c 2.2), [lit.[6,7] α_D^{19} − 11.1° (methanol, c 2.6)].

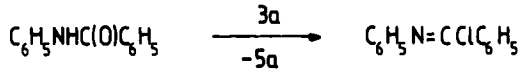
[f] Similar result was obtained when **3e** was used as a starting phosphine.

[g] The distilled product was contaminated with **5a**. Analytically pure sample isolated by GLC (5% OV 17).



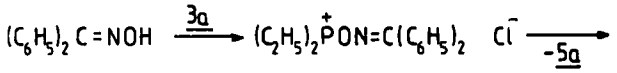
13; R=C_2H_5, X=S

SCHEME 10



16

SCHEME 11



15a

16

SCHEME 12

(entry 10, Table III) with acetic acid in the presence of **3a** leads to the formation of phenyl acetate and *N*-benzylacetamide, respectively, in satisfactory yields.

Summary

It has been demonstrated that the phosphines, R_2PCCl_3, can be used as convenient reagents for the preparation of new reactive phosphonium salts as well as reagents to promote chlorination, dehydration, and condensation reactions under very mild conditions.

EXPERIMENTAL

^{31}P-NMR spectra were recorded on a FT Jeol FX-60 spectrometer operating at 24.3 MHz using 85% H_3PO_4 as an external standard. ^{1}H-NMR spectra were taken on a Tesla BS 487C spectrometer using TMS as an internal standard. Diphenylphosphine[14] and dialkylphosphine ($R_1 = R_2 = C_2H_5$; *n*-C_3H_7, *n*-C_4H_9, *n*-C_8H_{17})[15] were prepared according to the reported procedures. Solvents and commercially available reagents were purified by conventional methods. All reactions were carried out under argon. Melting and boiling points are uncorrected.

Dialkyltrichloromethylphosphines **3a-d**; General procedure. Dialkylphosphine (R_1,R_2 = C_2H_5; *n*-C_3H_7; *n*-C_4H_9; *n*-C_8H_{17}; 0.1 mol) is added dropwise to the stirred solution of triethylamine (10.1 g, 0.1 mol), and carbon tetrachloride (16.8 g, 0.11 mol) in methylene chloride (90 ml) at 0°C. The reaction mixture is stirred at 0–5°C for 20 min and at room temperature for 45 min. Then dry ether (25 ml) is added to the mixture and the resulting mixture is cooled to 5°C. The precipitated triethylamine hydrochloride is filtered off and washed with ether. The combined filtrates are partly concentrated and used for further transformations. Yields and spectroscopic properties of **3a-d** are given in Table I.

Diphenyltrichloromethylphosphine (**3e**). Diphenylphosphine (1.86 g, 0.01 mol) is added dropwise to the stirred solution of triethylamine (1.01 g, 0.01 mol) and carbon tetrachloride (5 ml) in benzene (7 ml). Then the mixture is refluxed for 3 hr. After the mixture has been cooled to room temperature, dry ether (2.5 ml) is added and the resulting mixture is cooled to 5°C. The precipitated triethylamine hydrochloride is filtered off and washed with ether. The combined filtrates are evaporated under reduced pressure. The oily residue consists of **3e** slightly contaminated with diphenylchlorophosphine (5–15%, δ ^{31}P-NMR = 80 ppm), Yield and spectroscopic properties of **3e** are given in Table 1.

Hydrolysis of dialkyltrichloromethylphosphines **3a-d** *and diphenyltrichloromethylphosphine* **3e**; *General procedure.* Phosphines **3a-e** (10 mM) are added to a water-methanol (1:1/v:v) solution (10 ml) and set aside at room temperature for 12 h. The resulting solution is evaporated to leave the phosphine oxides **5a-e**. Yield: quantitative. Spectroscopic properties of **5a = d** were identical with those of authentic samples.[10] For analytical data and spectroscopic properties of **5e** see Table 2.

Reaction of diethyltrichloromethylphosphine (**3a**) *with electrophilic and nucleophilic reagents* (C_6H_5CHO, *HCl*, $(C_2H_5)_2NH$, Cl_2, H_2S); *General procedure.* To the stirred solution of diethyltrichloromethylphosphine (**3a**, 2.07 g, 0.01 mol) in dichloromethane (10 ml) a nucleophilic or an electrophilic reagent (0.01 mol) is added dropwise/or introduced as a gaseous stream and the mixture is set aside for 12 h at room temperature. The resulting mixture is evaporated and the residue distilled in vacuo (**7**) or recrystallized (**12a-c**). When H_2S is used as an electrophile, ethyl ether (10 ml) is added to the residue. The precipitated **12a** is filtered off and recrystallized. The etheral filtrate is evaporated to give crude **13**, which is purified by distillation. Yields, physical and spectroscopic data of **7**, **12a-c** and **13** are presented in Table 2.

Cycloelimination of 2,2-diethyl-4-phenyl-2,3,3-trichloro-1,2λ⁵ oxaphosphetane (**7**). The crude oxaphosphetane (**7**, 1.56 g, 0.005 mol) is heated in a sealed tube at 150°C for 0.5 h. The resulting mixture is subjected to destillation in vacuo to afford diethylphosphinyl chloride;
yield: 0.56 g (80%), b.p. 90%$_{0.3\ torr}$, ^{31}P-NMR (C_6H_6): δ = 74.0, lit.[16] δ = 74.8 and β,β-dichlorostyrene, yield: 0.64 g (74%), b.p. 224°C, lit.[17] b.p. 225°C.

Hydrolysis of 2,2-diethyl-4-phenyl-2,3,3-trichloro-1,2λ⁵oxaphosphetane (**7**). The crude oxaphosphetane (**7**, 1.56 g, 0.005 mol) is added to a water-methanol (1:1/v:v) solution (10 ml) and set aside at room temperature for 12 h. The resulting solution is evaporated to afford phosphine oxide (**10**);
yield: 1.26 g (86%), m.p. 136–137°C (petroleum ether), IR (KBr): 1165 cm^{-1} (P=O), ^{1}H-NMR ($CDCl_3$): 0.97–1.5 (6H, *m*, $^3J_{HH}$ = 8Hz, CH_3), 1.7–2.6 ('4H, *m*, $^3J_{HH}$ = 8Hz, CH_2), 5.4 (1H, *d*, $^3J_{PH}$ = 3.5 Hz, CH), 6.1 (1H, *s*, OH), 7.2–7.7 (6H, arom.), ^{31}P-NMR ($CHCl_3$): δ = 63 ppm.

Anal.	$C_{12}H_{17}Cl_2O_2P$	calc.	C 48.83	H 5.81	P 10.50
	(295.15)	found	49.05	5.85	10.40

Chlorination, dehydration and condensation reaction under influence of diethyltrichloromethylphosphine (**3a**) *and diphenyltrichloromethylphosphine* (**3e**); *General procedure.* To the stirred solution of the phosphine (0.01 mol), triethylamine (1.01 g, 0.01 mol) and dichloromethane (10 ml) the equimolar amount of an appropriate proton active substrate or substrates is added. The resulting mixture is set aside for 12 h at room temperature, or refluxed for 1.5 h, when **3a** or **3e** is used as a starting material, respectively. The solvent is then evaporated under reduced pressure and the products are isolated by distillation or crystallization. Their yields and physical data are reported in Table III.

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