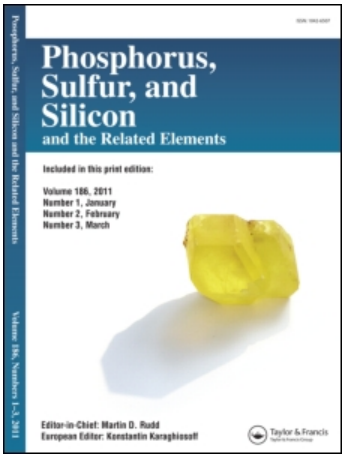

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Piotr Majewski[a]
[a] Institute of Organic Chemistry, Technical University, Łódź, Poland

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THE REACTION OF DIALKYLTRICHLOROMETHYLPHOSPHINES WITH METHYL ISOCYANATE AND WITH SATURATED AND α,β-UNSATURATED CARBONYL COMPOUNDS

PIOTR MAJEWSKI

Institute of Organic Chemistry, Technical University (Politechnika) Żwirki 36, PL-90924, Łódź 40, Poland

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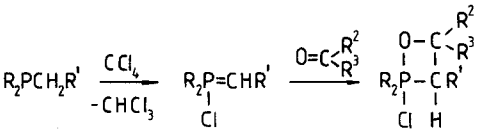
Diethyltrichloromethylphosphine (**4a**) reacts with methyl isocyanate (**6e**) and with nonenolizable saturated aldehydes, **6b–c**, to produce 1,2 λ^5-oxaphosphetanes, **7b–e**, whereas with enolizable saturated ketones, **6f, g**, it gives mixtures of cycloaddition products, **7f, g**, and vinyl chlorides, **14f, g**. By treatment with **4a**, 1,3-diketones **6h–j** are exclusively transformed into vinyl chlorides, **14h–j**. α,β-Unsaturated aldehydes, **6k, l**, react with **4a** to afford phosphine oxides **17k, l**. The crucial role of the oxaphosphetane type intermediates, **15k, l**, in the formation of **17k, l** has been demonstrated.

Key words: Diethyltrichloromethylphosphine; *P*-chlorodiethyldichloromethylenephosphorane; 1,2 λ^5-oxaphosphetane; saturated and α,β-unsaturated carbonyl compounds; diethyl-(1,1-dichloroalkyl)phosphine oxides.

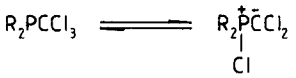
INTRODUCTION

It is well known that *P*-chloroylides, **1**, are readily accessible from the reaction of the alkylphosphines, **2**, and carbon tetrachloride.[1a,b,c] These ylides were found to be highly reactive towards carbonyl compounds giving oxaphosphetanes, **3**,[1a,2] (Scheme I).

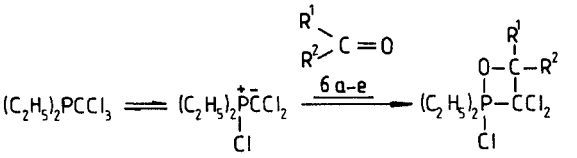
We have recently reported that the dialkyltrichloromethylphosphines **4**, which are chlorotropic tautomers of the ylides **5** (Scheme II), exhibit similar reactivity. Diethyltrichloromethylphosphine (**4a**) reacts readily with benzaldehyde (**6a**) forming 1,2λ^5-oxaphosphetane **7a**[3] (Scheme III). However, the reaction with acetylacetone follows different pathway producing the corresponding β-chlorovinylketone.[3]



SCHEME I



SCHEME II



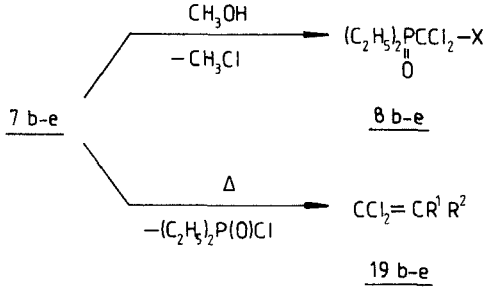
SCHEME III

TABLE I

1,2 λ^5-oxaphosphetanes, **7b–e**

7	Yield [a] %	b.p. (°C)/torr	Molecular formula	^{31}P-NMR (ppm)	^{1}H-NMR (ppm), J(Hz)
b	87	b	$C_{12}H_{15}Cl_3NO_3P$ (358.6)[c]	-2.1 (C_6D_6)	(C_6D_6),1.45 (6H,dt,$^3J_{PH}$=24, $^3J_{HH}$=7, $PCH_2\underline{CH_3}$),2.4-3.1 (4H,m,$PC\underline{H_2}CH_3$),5.38 (1H,d, $^3J_{PH}$=2, OCH),7.5-8.5 (4H,arom.).
c	85	71-72/0.4	$C_7H_{11}Cl_6OP$ (354.8)[d]	-9.6 ($CDCl_3$)	($CDCl_3$),0.9-1.8(6H,m,$PCH_2\underline{CH_3}$), 2.3-3.1(4H,m,$PC\underline{H_2}CH_3$),4.9(1H, d,$^3J_{PH}$=4.5, $CHCCl_3$)
d	78	80-82/0.3	$C_{10}H_{20}Cl_3OP$ (293.6)[d]	-4.7 (C_6H_6)	(C_6D_6), 0.8-1.5(6H,m,$PCH_2\underline{CH_3}$), 1.1[9H,s,$CH(\underline{CH_3})_3$],2.0-3.1 (4H,m,$PC\underline{H_2}CH_3$), 3.8[1H,d,$^3J_{PH}$=2, $C\underline{H}(CH_3)_3$].
e	83	b	$C_7H_{13}Cl_3NOP$ (264.5)[c]	-31.8 (C_6D_6)	(C_6D_6), 1.2(6H,dt,$^3J_{PH}$=26, $^3J_{HH}$=7, $PCH_2\underline{CH_3}$), 2.0-2.9 (4H,m,$PC\underline{H_2}CH_3$), 2.6 (3H,s,CH_3N).

[a]Estimated from the integrated intensities of the ^{31}P-NMR peaks of the crude product.
[b]Oxaphosphetane undergoes thermal decomposition during distillation to give cycloelimination products.
[c]Microanalysis has not been performed.
[d]Satisfactory microanalyses obtained: C ± 0.35, H ± 0.25, P ± 0.25.



8	b	c	d	e
X	$C(OH)C_6H_4NO_2$-p	$C(OH)CCl_3$	$C(OH)C(CH_3)_3$	$C(=O)NHCH_3$

19	b	c	d	e
R^1	H	H	H	
				$=NCH_3$
R^2	$C_6H_4NO_2$-p	CCl_3	$C(CH_3)_3$	

SCHEME IV

RESULTS AND DISCUSSION

This paper describes our further studies on dichotomy of the reaction between the phosphines **4** and different saturated and α, β-unsaturated carbonyl compounds. Using diethyltrichloromethylphosphine (**4a**) as a model starting material we have shown that its reaction with such nonenolizable aldehydes as *p*-nitro-benzaldehyde (**6b**), chloral (**6c**) and pivalaldehyde (**6d**), and also with methyl isocyanate (**6e**), in benzene at room temperature affords 1,2λ^5-oxaphosphetanes **7b–c** (Scheme 3). The yields, physical constants and spectroscopic data of the obtained compounds are presented in Table I.

The oxaphosphetanes **7b–e** are termally unstable and sensitive to moisture and hydroxylic reagent. Subjected to heating they undergo cycloelimination to afford olefins and diethylphosphinic chloride in good yields, whereas on treatment with methanol they give exclusively diethyl-(1,1-dichloroalkyl)phosphine oxides **8b–e** (Scheme IV). Physical constants and spectroscopic date of **8b–e** are shown in Table II.

The enolizable carbonyl compounds, which exist mostly in a carbonyl form, like cyclopentanone (**6f**) and cyclohexanone (**6g**) react with the phosphine **4a** to give the chlorination, **14f, g**, and cycloaddition products, **7f, g** (**7f** and **7g** show 31 P. chemical shifts of δ = 6.1 and 6.3 ppm, respectively).[4] The chlorination is a little more favored pathway affording vinyl chlorides in 25–49% yield (Table III). The addition products, **7f, g**, are not enough stable and undergo secondary reactions. Thus, when cyclopentane is a substrate, a mixture of phosphine oxides was formed ($\delta_{31}p$ = 56.5, 57.4 and 60.2 ppm) however with cyclohexanone (**6g**) E-3-[chloro(diethylphosphoryl)-methylene]cyclohexene (**11**)[5] was produced as a main

TABLE II

Diethyl-(1,1-dichloro-2-hydroxyalkyl)phosphine oxides, **8b–e**, and *N*-methyl dichloro(diethylphosphinyl)acetamide (**8e**)

8	Yield %	m.p.(°C) or b.p. (°C)/+torr	Molecular formula[a]	IR(KBr) νcm^{-1}	^{31}P-NMR (ppm)	^{1}H-NMR (ppm), J(Hz)
b	92	192 (petroleum ether)	$C_{12}H_{16}Cl_2NO_4P$ (340.1)	1180 (P=O)	66.0 ($CDCl_3$)	($CDCl_3$), 0.7-1.65 (6H,m,$PCH_2\underline{CH_3}$), 1.8-2.7 (4H,m,$P\underline{CH_2}CH_3$), 5.5 (1H,d,$^3J_{PH}$=2, $\underline{CH}OH$), 6.4 (1H,s,OH)
c	86	133-134 (acetonitryl)	$C_7H_{12}Cl_5O_2P$ (336.3)	1180 (P=O)	68.8 (CH_3OH)	(DMSO-d_6), 1.2 (6H, dt,$^3J_{PH}$=18,$^3J_{HH}$=8, $PCH_2\underline{CH_3}$), 1.7-2.7 (4H,m,$P\underline{CH_2}CH_3$), 5.0 (1H,d,$^3J_{PH}$=2.3,$CHCCl_3$), 6.8 (1H,br.s,OH)
d	95	141-142 (petroleum ether)	$C_{10}H_{21}Cl_2O_2P$ (275.1)	1180 (P=O)	65.8 ($CDCl_3$)	($CDCl_3$), 0.95-1.7 (6H,m,$PCH_2\underline{CH_3}$), 1.7-2.7 (4H,m, $P\underline{CH_2}CH_3$), 4.1 |1H, d,$^3J_{PH}$=3; $\underline{CH}(CH_3)_3$| 5.3 ($1H_{br.s}$,OH)
e	94	146-148/0.6	$C_7H_{14}Cl_2NO_2P$ (246.0)	(film) 1170 (P=O)	61.3 ($CDCl_3$)	($CDCl_3$), 1.2 (6H, dt,$^3J_{PH}$=18,$^3J_{HH}$=7, $PCH_2\underline{CH_3}$), 1.6-2.6 (4H,m,$P\underline{CH_2}CH_3$),2.85-2.95 (3H,2s,$NHC\underline{H_3}$), 7.5 (1H,br.s,NH).

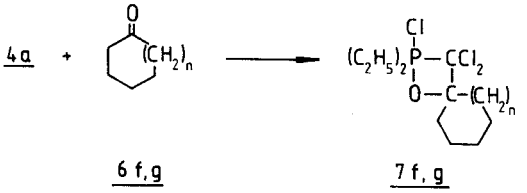
product. The formation of the product **11** is best explained by assuming that the intermediates **7g** is involved in the corresponding reaction sequences (Scheme V). The reaction of the phosphine **4a** with highly enolyzed carbonyl compounds such as 1,3-diketones, **6h–j**, is chemoselective and leads exclusively to the formation of the corresponding vinyl chlorides **14h–j** (Scheme VI).

An important factor controlling the chlorination process is undoubtedly the stability of the intermediate anion **13**. The obtained results are collected in Table III. It is noteworthy that similar chlorination has been observed with the Ph_3P/CCl_4 system **6a, b** being an analogue of the phosphine **4a**.

The reaction of the phosphine **4a** with crotonic (**6k**) and cynamic (**6l**) aldehydes representing α, β-unsaturated carbonyl compounds leads to the formation of 1,2-

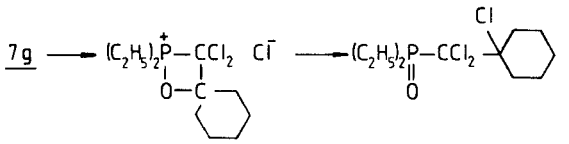
TABLE III
Vinyl chlorides **14 f–j**

Sterting carbonyl compound 6	Vinyl chloride 14	Yield (%)	b.p. (°C)/torr
h	h	92	80-82/12 lit.[6b] 34-35/1.5
i	i	90	80-83/6 lit.[6b] 83-85/7
j	j	86	61-63/7 lit.[6b] 74-76/12
f	f	25	43-45/30 lit.[13] 102-103/760
g	g	49	64-65/45 lit.[14] 35/13



6 f,g 7 f,g

6,7 f g
n 0 1



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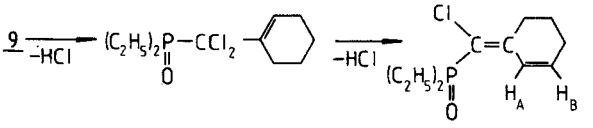
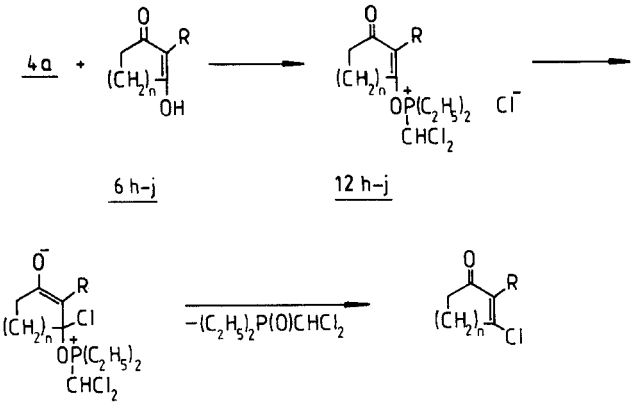


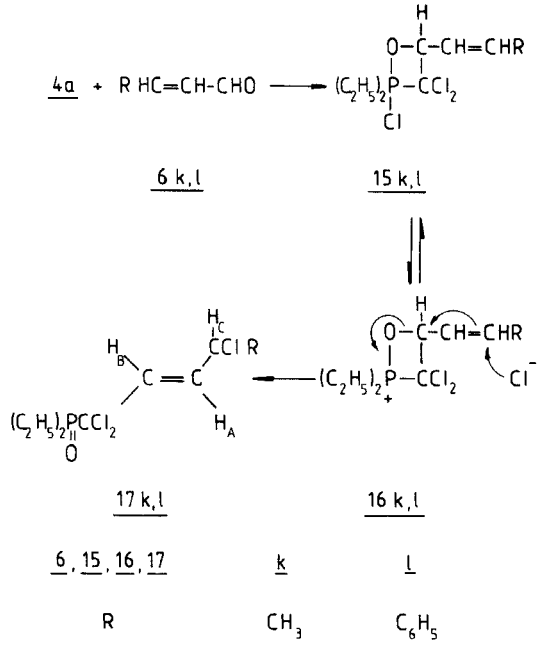
10 11

SCHEME V



6, 12, 13, 14	h	i	j
n	1	2	2
R	CH_3	CH_3	H

SCHEME VI



6, 15, 16, 17	k	l
R	CH_3	C_6H_5

SCHEME VII

cycloadducts with the oxaphosphetane ring, **17k, l**, (Scheme VII). These compounds, however, were unsufficiently stable to be isolated. On standing at room temperature they are spontaneously converted into phosphine oxides **17k, l**. The formation of **15k, l** has been unambiguously confirmed by means of ^{31}P-NMR (**17k**

and **17l** show $\delta_{31}p = -3.9$ ppm and -3.8 ppm, respectively[4]). The transformation of **15k, l** into **17k, l** involves presumably the dissociation of **15k, l** providing the phosphonium salt **16k, l** which is then stabilized by S_N2' type dealkylation (Scheme VII). The compounds **17k, l** were characterized by ^{1}H- and ^{31}P-NMR, IR and had satisfactory microanalytical data.

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. IR spectra were recorded on an IR-225 (Perkin-Elmer) spectrophotometer.

Diethyltrichloromethylphosphine (**4a**)[3] was prepared according to the reported procedure. All reaction were carried out under argon. Melting and boiling points are uncorrected.

*Reaction of diethyltrichloromethylphosphine (**4a**) with aldehydes **6b–d, k, l** and methyl isocyanate (**6e**). General procedure:* To the stirred solution of diethyltrichloromethylphosphine (**4a**) (20.7 g, 0.01 mol) in dichloromethane (10 ml) a carbonyl compound (0.01 mol) was added dropwise and the mixture was set aside for 18 h at room temperature. Dichloromethylene was evaporated from the reaction mixture under reduced pressure to give, when starting materials were **6b–e**, oxaphosphetanes **7b–e**. Only oxaphosphetanes **7c, d** were purified by distillation in vacuo. Thermally unstable oxaphosphetanes, **7b, e**, were sufficiently pure to be used for further transformations. Yields, physical and spectroscopic data of **7b–e** are presented in Table I.

Reaction of aldehydes, **6k, l**, with **4a** resulted in the formation of two products, unstable oxyphosphetane, **15k, l**, and phosphine oxide, **17k, l**. Distillation of these mixtures in vacuo afforded only the phosphine oxide, **17k, l**.

17k; yield: 1.41 g (51%), b.p. 151–155°C/0.4 torr, oil, IR(film): 1190 cm^{-1} (P = O). ^{31}P-NMR ($CHCl_3$): δ = 57.8. ^{1}H-NMR (CD_3CN) δ: 1.13 (6H, dt, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17 Hz, $C\underline{H}_3CH_2P$), 1.57 (3H, d, $^3J_{HH_C}$ = 6.7 Hz, $C\underline{H}_3CH_CCl$), 1.6–2.2 (4H, m, $^3J_{HH}$ = 7.5 Hz, $C\underline{H}_2P$), 4.75 (1H, m, $^3J_{HH(CH_3)}$ = 6.7 Hz, $^3J_{H_AH_C}$ = 7.0 Hz, H_C), 6.18 (1H, m, $^3J_{H_BH_A}$ = 14.8 Hz, $^3J_{PH}$ = 2.3 Hz, H_B), 6.36 (1H, m, $^3J_{H_AH_B}$ = 14.8 Hz, $^3J_{H_AH_C}$ = 7.0 Hz, $^4J_{PH}$ = 2.0 Hz, H_A).

Anal. $C_9H_{16}Cl_3OP$ calc.: C 38.94 H 5.81 P 11.16
(277.57) found: 38.70 5.70 11.05

17l; yield: 1.66 g (49%), b.p. 163–165°C/0.3 torr, oil, IR(film): 1190 cm^{-1} (P = O). ^{31}P-NMR($CHCl_3$): δ = 58.0. ^{1}H-NMR($CDCl_3$) δ: 1.2 (6H, m, $^3J_{PH}$ = 17 Hz, $^3J_{HH}$ = 7 Hz, $CH_2C\underline{H}_3$), 1.6–2.4 (4H, m, $^3J_{HH}$ = 7 Hz, $C\underline{H}_2CH_3$), 5.55 (1H, d, $^3J_{H_AH_C}$ 7 Hz, Hc), 6.30 (1H, m, $^3J_{H_AH_B}$ = 14.5 Hz, $^3J_{PH_B}$ = 2.5 Hz, H_B), 6.53 (1H, m, $^3J_{H_AH_B}$ = 14.5 Hz, $^3J_{H_AH_C}$ = 7 Hz, $^4J_{PH}$ = 2 Hz, H_A), 7.2–7.5 (5H arom.)

Anal. $C_{14}H_{18}Cl_3OP$ calc.: C 49.50 H 5.34 P 9.12
(339.63) found: 49.53 5.20 9.00

*Reaction of diethyltrichloromethylphosphine (**4a**) with ketones **6f, g**. General procedure:* A solution of diethyltrichloromethylphosphine (**4a**) (2.07 g, 0.01 mol) in dichloromethane (10 ml) was added dropwise to a stirred solution of ketone, **6k, l**, (0.01 mol) in dichloromethane (5 ml) at 20°C and the mixture was set aside for 96 h at room temperature. Then dichloromethane was evaporated from the reaction mixture to give vinyl chloride, **14f, g**, dichloromethyldiethylphosphine oxide (**18**), cyclo-addition product, **7f, g**, and the corresponding mixtures of phosphine oxides. These reaction mixtures were distilled in vacuo to give vinyl chloride, **14f, g**, and the mixture of phosphine oxides in the molar ratio 5:1:1 (^{31}P: 64.9, 60.9 and 58.3 (ppm)) and ~1:1:1 (^{31}P: 60.2, 57.4 and 56.5 (ppm)) from **6g** and **6f**, respectively. Yields and b.p.'s of **14f, g** are given in Table III. The phosphine oxide **11** has been isolated from the mixture of phosphine oxides obtained from **6g** by column chromatography (silica gel, EtOAc as eluent); yield: 0.74 g (32%), oil, IR(film): 1180 cm^{-1} (P = O), ^{31}P-NMR ($CHCl_3$) δ: = 64.9, ^{1}H-NMR($CDCl_3$) δ: 0.8–2.7 [16H, overlapped multiplets of cyclohexenyl (6H) and ethyl moiety (10H)], 5.8–6.35 (1H, m, $^3J_{H_AH_B}$ = 10.5 Hz, H_B), 7.65 (1H, dt, $^3J_{H_AH_B}$ = 10.5 Hz, $^4J_{HH}$ = 1.8 Hz, H_A).

Anal. $C_{11}H_{18}ClOP$ calc.: C 57.77 H 7.79 P 13.31
(232.68) found: 57.60 7.65 12.35

*Reaction of diethyltrichloromethylphosphine (**4a**) with diketones **6h–j**. General procedure:* A solution of diethyltrichloromethylphosphine (**4a**) (2.07 g, 0.01 mol) in dichloromethane (10 ml) was added

dropwise to a stirred solution of diketone, **6h–j**, (0.01 mol), in dichloromethane (5 ml) at 20°C and the mixture was set aside for 12 h at room temperature. Then dichloromethane was evaporated from the reaction mixture to afford vinyl chloride, **14h–j**, and the phosphoroorganic by-product dichloromethyldiethylphosphine oxide (**18**). Vinyl chlorides, **14h–j**, were isolated by distillation in vacuo. Their yields and b.p.'s are given in Table III.

Methanolysis of 1,2λ⁵-oxaphosphetane **7b–e**. Oxaphosphetane **7b–e** (0.005 mol) was added to methanol (10 ml) and set aside at room temperature for 12 h. The resulting solution was evaporated to afford phosphine oxide **8b–e**, which was purified by recrystallization or distillation. Yields, physical and spectroscopic data of **8b–e** are presented in Table II.

Cycloelimination of 1,2λ⁵-oxaphosphetane **7b–e**. Oxaphosphetane **7b–e** (0.005 mol) was heated under argon at 150°C for 0.5 h. The resulting mixture was distilled in vacuo to afford diethylphosphinyl chloride; yield: 0.44–0.56 g (70–80%), b.p. 90°C/0.3 torr, ^{31}P-NMR(C_6H_6): δ = 75 ppm, lit.[7] δ = 74.8 ppm and olefine **19b–c**, which was purified by redystillation or crystallization. **19b**: yield: 0.87 g (80%), m.p. 86–87°C, lit.[8] 89°C. **19c**: yield: 0.75 g (70%), b.p. 175°C, lit.[9] 177–179°C. **19d**: yield: 0.59 g (76%), b.p. 130–133°C, lit.[10] 134°C, lit.[11] 55–56/39 **19e**: yield: 0.44 g (71%), b.p. 25–30°/20 torr. This compound spontaneously hydrolyzed with moisture to give *N*-methyl dichloroacetamide: m.p. 76–78°C, lit.[12] m.p. 78°C.

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