state is again in accordance with the idea that ring closure to a diaziridine is favoured in the first excited state as also indicated by the PPP calculation.

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176. Organic Phosphorus Compounds 53

Preparation and Properties of Bis-(chloromethyl)-phosphinic and -thiophosphinic Acid Derivatives as well as Tertiary Phosphine Oxides and Sulfides Containing two $ClCH_2$ Groups [1]

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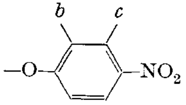
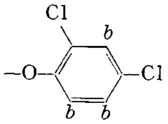
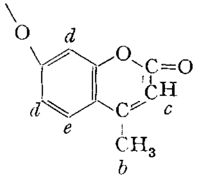
(27. V. 71)

Summary. Bis-chloromethyl-phosphinates, -thiophosphinates, and -phosphinic amides are formed in fair yield by treating either bis-chloromethyl-phosphinic or -thiophosphinic chloride with alcohols, thiols, or amines in the presence of equivalent amounts of acid binding agents. Unexpectedly, the thiophosphinates show no insecticidal activity and only the β-cumaryl derivative exhibits a low herbicidal activity.

Reduction of bis-chloromethyl-thiophosphinic chloride to bis-chloromethyl-phosphinous chloride is effected with $(PhO)_3P$ at 170°. Interaction of this chloride, $(ClCH_2)_2PCl$, with *Grignard* reagents yields tertiary phosphines, which at slightly above room temperature are unstable, but which may be characterized as oxides or sulfides.

We [2] and others [3] [4] have recently found an easy method for the synthesis of bis-chloromethyl-phosphinic chloride involving reaction of $(HOCH_2)_2P(O)OH$ with excess $SOCl_2$ at 80° [3] [2], or with PCl_5 [4]. This chlorination with $SOCl_2$ effected at room temperature, however, unexpectedly affords bis-chloromethyl-phosphinic anhydride in high yield. Further study of this chlorination shows that the anhydride is also obtained, even at 80°, when only stoichiometric amounts of $SOCl_2$ are used. At room temperature the rate of reaction of the anhydride with $SOCl_2$ is extremely slow,

Table 1. *Physical properties of bis-(chloromethyl)-phosphinates,* $(\overset{a}{ClCH_2})_2P(O)X$

X	Yield in %	m.p. (b.p.) °C (solvent for crystn.)	solvent ¹H-NMR.	¹H-NMR. in ppm (coupl. const. in Hz)				³¹P-chem. shift in ppm (H_3PO_4 as ref.)
				a ($ClCH_2$)	*b*	*c*	*d*	
–Cl	85.6	(66–72°/0.1 Torr)	$CDCl_3$	4.08 (J_{PCH} = 7.2)				– 49.3 (neat)
	53.5	66–67° (Et_2O/hexane)	$CDCl_3$	3.95 (J_{PCH} = 8.2)	7.45 (J_{HH} = 9)	8.25 (J_{HH} = 9)		– 39.6 (in $CDCl_3$)
		52.5–53° ($CHCl_3$/hexane)	$CDCl_3$	3.92 (J_{PCH} = 8.2)	7.3 (*m*)			– 41.6 (in $CHCl_3$)
		140–142° (acetone/hexane)	$CDCl_3$/ CD_3OD	3.96 (J_{PCH} = 8.2)	2.4 (J_{HH} = 1)	6.06 (J_{HH} = 1)	6.8 [a] (*m*)	
$–N(\underset{b}{CH_3})_2$	18.6	79.5–80° [b] (benzene)	$CDCl_3$	3.79 (J_{PCH} = 7)	2.78 (J_{PNCH} = 9)			– 35.1 ($CHCl_3$)
$–N(\underset{c}{CH_2}\underset{b}{CH_3})_2$	54.5	62.9–63.3° [c] (Et_2O)	$CDCl_3$	3.73 (J_{PCH} = 7)	1.16 (J_{HH} = 7)	3.18 (J_{HH} = 7, J_{PNCH} = 10.5)		– 34.2 ($CHCl_3$)

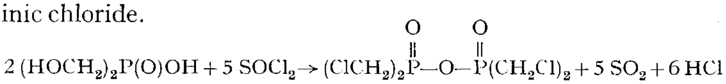
[a] *e* at 7.48 ppm (*m*, 1 H).

[b] Lit. [4], m.p. 80–81°.

[c] Lit. [4], m.p. 64–65°.

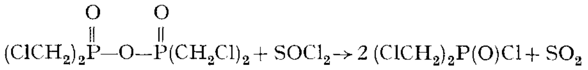
thus even excess $SOCl_2$ produces only the anhydride, if the temperature is kept below 20°C. At higher temperatures (~80°) the anhydride is cleaved by $SOCl_2$ to give bis-chloromethyl-phosphinic chloride.

These experiments suggest that the chlorination of $(HOCH_2)_2P(O)OH$ with $SOCl_2$ proceeds in two steps: a) formation of the anhydride, b) transformation of the latter to phosphinic chloride.



$$2\,(HOCH_2)_2P(O)OH + 5\,SOCl_2 \rightarrow (ClCH_2)_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{O}{\overset{\|}{P}}(CH_2Cl)_2 + 5\,SO_2 + 6\,HCl$$

Ia



$$(ClCH_2)_2\overset{O}{\overset{\|}{P}}{-}O{-}\overset{O}{\overset{\|}{P}}(CH_2Cl)_2 + SOCl_2 \rightarrow 2\,(ClCH_2)_2P(O)Cl + SO_2$$

I

Conversion of bis-chloromethyl-phosphinic chloride to the corresponding thioderivative is readily achieved with P_2S_5 [5] [6]:

$$5\,(ClCH_2)_2P(O)Cl + P_2S_5 \rightarrow 5\,(ClCH_2)_2P(S)Cl + P_2O_5$$

This thiophosphinic chloride as well as several of its esters – but not all – show in the ^{1}H-NMR. spectrum nonequivalence of the protons within the CH_2-groups and give an A_2B_2X spectrum [Fig.]. The corresponding bis-chloromethyl-phosphinic chloride, its esters, bis-chloromethyl-alkyl-phosphine sulfides, their corresponding oxides, and the thio-amide $(ClCH_2)_2P(S)NEt_2$ do not exhibit such spectra. Although several esters of bis-chloromethyl-phosphinic acid ([2] and ref. cited there) and -thiophosphinic acid [5] have been described in the litterature, the esters containing a substituted phenoxy group or the β-cumaryl residue are unknown. They have now been prepared by conventional methods from the acid chlorides with either the sodium phenolates or thiophenolates, or with phenols in the presence of a tertiary amine (see Tables 1 and 2).

$$(ClCH_2)_2P(Y)Cl + NaXR \rightarrow (ClCH_2)_2P(Y)XR + NaCl$$

$$Y = O, S,\ X = O, S,\ R = 4{-}NO_2C_6H_4,\ 4\text{-}FC_6H_4,\ 4{-}ClC_6H_4,\ \beta\text{-cumaryl}$$

Unexpectedly, the thiophosphinates showed no insecticidal activity and no, or only very low (*e.g.*, $(ClCH_2)_2P(S)O$-β-cumaryl), herbicidal activity.

Reduction of bis-chloromethyl-thiophosphinic chloride with triphenylphosphite [7] gave bis-chloromethyl-phosphinous chloride (XV) [6] [8] in 60% yield.

$$(ClCH_2)_2P(S)Cl + (PhO)_3P \rightarrow \underset{(XV)}{(ClCH_2)_2PCl} + (PhO)_3PS$$

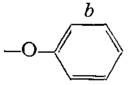
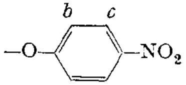
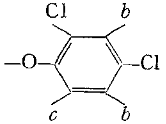
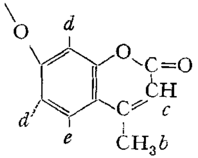
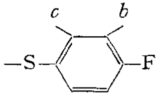
Reaction of this chloride XV with alkyl or aryl *Grignard* reagents at –20° in ethereal solution, gave high yields of bis-chloromethyl-alkyl-, or -aryl-phosphines as evidenced by the isolation of $(ClCH_2)_2PEt$ as oxide in 77.6% yield after oxidation with bromine.

$$(ClCH_2)_2PCl + RMgBr \rightarrow (ClCH_2)_2PR + MgClBr$$

Like $ClCH_2PPh_2$ [10] these phosphines also seem to be not very stable. Thus when a sample of $(ClCH_2)_2PEt$ was distilled under reduced pressure at 85°/20 Torr, it solidified and then showed in the NMR. spectrum signals for $P{-}CH_3$ and PCH_2P groups.

Likewise, when a sample of $(ClCH_2)_2PPh$ was heated to remove benzene and bromobenzene after hydrolysis (see expl.) it then showed in the ^{1}H-NMR. spectrum signals

Table 2. *Physical Properties of bis-chloromethyl thiophosphinates* $(Cl\underset{a}{CH_2})_2P(S)X$

X	Yield in %	m.p. (b.p.) °C (solvent for crystn.)	solvent ¹H-NMR.	¹H-NMR. in ppm (coupl. const. in Hz)			³¹P-chem. shift in ppm (H_3PO_4 as ref.)
				a	*b*	*c*	
–Cl	60	(46–48°/0.7 Torr)[a]	$CDCl_3$	4.12 (J_{PCH} = 4.87, (nonequivalence)			– 81.9 (neat)
	25.5	54.5–55° (Et_2O/hexane)[b]	$CDCl_3$	3.97 (nonequivalence)	7.25 (*m*)		– 87.0 ($CHCl_3$)
	57.5	76.0–76.3° ($CHCl_3$/hexane)	$CDCl_3$	4.05 (J_{PCH} = 6)	7.29 (J_{HH} = 9, J_{POCCH} = 1.5)	8.25 (J_{HH} = 9)	– 88.5 ($CHCl_3$)
	32.5	51.8–52.2° (Et_2O/hexane)	$CDCl_3$	4.08 (J_{PCH} = 6) (nonequivalence)	7.2 (*m*)	7.42 (*m*)	– 89.9 ($CHCl_3$)
	48.1	120–121° ($CHCl_3$/hexane)	$CDCl_3$	4.04 (J_{PCH} = 6)	2.4 (J_{HH} = 1)	6.25[c][d] (J_{HH} = 1)	– 88.6 ($CHCl_3$)
		50.0–50.5° ($CHCl_3$/hexane)	$CDCl_3$	3.94 (J_{PCH} = 5)	7.1 (J_{HH} = 8.7) (J_{FH_b} = 8.7)	7.5 (J_{HH} = 8.7) (J_{FH_c} = 5.1, J_{PSCCH} = 2)	– 70.2 ($CHCl_3$)
$–N(\underset{c}{CH_2}\underset{b}{CH_3})_2$		liquid	$CDCl_3$	3.88 (J_{PCH} = 5.5)	1.16 (J_{HH} = 7)	3.28 (J_{HH} = 7, J_{PNCH} = 12.5)	– 62.4 ($CHCl_3$)

[a] Lit. [5] b.p. 104–106°/10 Torr.

[b] Lit. [5] m.p. 56–57°.

[c] *d* at 7.22 ppm (*m*, 2 H).

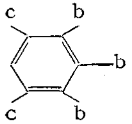
[d] *e* at 7.6 ppm (*m*, 1 H).

Table 3. *Physical properties of bis-chloromethyl-phosphinous derivatives* $(\overset{a}{ClCH_2})_2PX$

X	Yield in %	b.p. °C	^1H-NMR. in ppm (coupl. const. in Hz)		^{31}P-chem. shift in ppm (H_3PO_4 as ref.)
			a	*b*	
–Cl	61	45–47°/10 Torr[a]	3.93 (nonequivalence of H)		–71.9 (subst.)
$\underset{b}{CH_3}$	28.8	44°/5Torr	3.72 (J_{PCH} = 6.3)	1.19 (J_{PCH} = 3.6)	
–CH_2CH_3	23	85°/20–22 Torr			

[a] Lit. [6]: b.p. 74–77°/16–18 Torr; [8]: b.p. 76°/22 Torr.

Table 4. *Physical properties of oxides and sulfides* $(\overset{a}{ClCH_2})_2P(Y)R$

R	Y	m.p. °C	solvent ^1H-NMR.	^1H-NMR. in ppm (coupl. const. in Hz)			^{31}P-chem. shift in ppm (H_3PO_4 as ref.)
				a	*b*	*c*	
–$\underset{b}{CH_3}$	S	yellow oil	$CDCl_3$	3.84 (J_{PCH} = 6)	1.19 (J_{PCH} = 12.8)		
$\underbrace{CH_2CH_3}_{b}$	S	30.5–31° (from Et_2O/hexane)	$CDCl_3$	3.8 (J_{PCH} = 5.8)	0.95–2.45 (*m*)		–55.2 ($CHCl_3$)
$\underbrace{CH_2CH_3}_{b}$	O	42.5–43°[a]	$CDCl_3$	3.77 (J_{PCH} = 6.8)	1.28–2.06		–45.7 ($CHCl_3$)
	S	41–41.5° (Et_2O/hexane)	$CDCl_3$	4.05 (J_{PCH} = 5.4)	7.55 (*m*)	8.0 (*m*)	–44.2 ($CHCl_3$)

[a] Lit. [9] m.p. 42–44°.

for PCH_3, two different $ClCH_2P$ groups, PCH_2P and P–Ph groups. The phosphine $(ClCH_2)_2PCH_3$ could, however, be distilled at 44°/5 Torr without decomposition. Obviously these bis-chloromethyl-phosphines undergo dimerization and/or polymerization reactions similar to those of diphenyl-chloromethyl-phosphine, see [10].

Therefore these phosphines were isolated and identified either as sulfides or as oxides (see Tables 3 and 4).

$$(ClCH_2)_2RP + S\ (\text{or } Br_2/H_2O) \rightarrow (ClCH_2)_2RP \rightarrow S\ (\text{or } \rightarrow O)$$

Experimental Part[1])

(with Messr. *A. Hauser* and *A. Zoller*)

A. $(ClCH_2)_2P(O)Cl$ and Derivatives. – *1. Preparation of* $(ClCH_2)_2P(O)Cl$ (I): 415 g (91.5%) (I) were prepared by reaction of 315 g of $(HOCH_2)_2P(O)OH$ with 1785 g of $SOCl_2$ as described previously [2]; using only stoichiometric amounts of $SOCl_2$ the anhydride Ia, instead of the chloride I, was obtained.

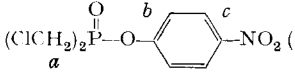
a) $(ClCH_2)_2P(O)O(O)P(CH_2Cl)_2$ (Ia) is obtained when 472 g (3.75 moles) of anhydrousi $(HOCH_2)_2P(O)OH$ is added in *small portions*, over a period of 6 h with stirring to 1335 g (11.25 moles) of $SOCl_2$; if addition is too fast, strong foaming sets in. Continous evolution of HCl and SO_2 is observed; the reaction is endothermic. The mixture is stirred for a further 3 h and then heated in vacuum to 70° to remove volatile products, giving 529.1 g (92%) crude Ia.

54.1 g crude Ia yield on fractionation 44.2 g (82%) pure Ia, b.p. 185°/0.1 Torr, which solidifies on cooling, m.p. 70–72° (Lit. [2] b.p. 205°/2 Torr, m.p. 74°). H^1-NMR. (in $CDCl_3/ClCH_2$) at 3.72 ppm (J_{PCH} = 9 Hz). The rest of crude Ia (475 g) is suspended in 1 l. CCl_4, stirred and treated with 321 g PCl_5 over a period of 1.5 h. An exothermic reaction ensues and a dark colored solution is obtained which is stirred at room temperature for 1.5 h and then heated under reflux for one hour. Fractional distillation yields 480.4 g (85.6%) pure I, b.p. 66–72°/0.1 Torr, n_D^{20} = 1.5193 (Lit. [2, 3] b.p. 98–101°/1 Torr, n_D^{25} = 1.5196). The ^{31}P-chem. shift[3]) of –51.6 ppm (Lit. [5] –49.3 ppm), and the H^1-NMR. spectrum[3]) (see table 1) confirm the structure assigned. $C_2H_4Cl_3OP$ (181.4): eq. wt. found 180.4.

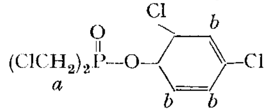
b) Prep. of Ia at 80° with stoichiometric amount of $SOCl_2$: To 133.5 g (1.12 moles) of boiling $SOCl_2$, under reflux 47.2 g (0.374 mole) of $(HOCH_2)_2P(O)OH$ (containing 3.6% $HOCH_2P(O)(OH)_2$) is slowly added. After heating for 5 h at 80°, the mixture yields on distillation 44.2 g (77%) Ia, b.p. 176–182°/0.01 Torr, m.p. 68–73°.

c) Prep. of Ia with excess $SOCl_2$ at 0 to 10°: 46.2 g (0.367 mole) of $(HOCH_2)_2P(O)OH$ is added slowly to 218 g (1.835 moles) of $SOCl_2$ over a period of 5 h at 0–20°. After stirring for 3 h at room temperature, distillation yields first excess $SOCl_2$ and then a forerun (15.3 g) containing $(ClCH_2)_2P(O)Cl$ and finally 35.0 g (62%) Ia, b.p. 176–182°/0.01 Torr, m.p. 68–73°.

d) Cleavage of Ia with $SOCl_2$ at 80°: 4.4 g (0.0144 mole) Ia and 20 g (6.168 mole) $SOCl_2$ are heated to 80° (at room temperature very low rate of reaction). SO_2 is continously evolved. After 2 h, distillation gives excess $SOCl_2$ and a quantitative yield of I b.p. 103–105°/6 Torr.

2. 

$(ClCH_2)_2P(O)–O–C_6H_4–NO_2$ (II). From 3 g (0.0165 mole) I, 2.65 g (0.0165 mole) *p*-$NO_2C_6H_4ONa$ in 70 ml tetrahydrofuran (THF.) After 1 h heating under reflux, NaCl is filtered off, filtrate is evaporated and residue recrystallized from Et_2O/hexane to give 2.5 g (53.5%) II, m.p. 66–7°.

3. 

$(ClCH_2)_2P(O)–O–C_6H_3Cl_2$ (III). As in *2*, I (3 g) gives 1.9 g III, m.p. 52.5–3° (from $CHCl_3$/hexane). ^{31}P-41.6 ppm (in $CHCl_3$, trace of impurity at –35.2 ppm).

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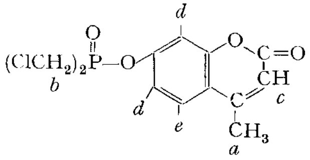
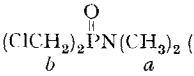
[1]) Analyses by *A. Peisker-Ritter* and *H. Wolf*, Brugg AG, and by *A. Manser*, ETH Zürich. – ^1H-NMR. data see tables.

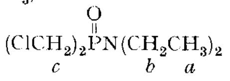
[2]) ref. 85% H_3PO_4.

[3]) ref. $(CH_3)_4Si$.

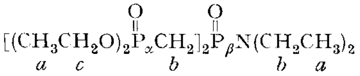
4. 

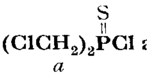
(IV). As in *2*, I (3 g) gives a low yield of IV, m.p. 140–2° (from acetone/hexane).

5. 
$\underset{b}{(ClCH_2)_2}\overset{O}{\overset{\|}{P}}\underset{a}{N(CH_3)_2}$ (V), 27.2 g (0.15 mole) I with 13.5 g (0.3 mole) $(CH_3)_2NH$ and 400 ml Et_2O as in *2*, gives 5.1 g (18.6%) V, m.p. 79.5–80° (from benzene) (Lit. [4] m.p. 80–1°). ^{31}P-35.1 ppm (in $CHCl_3$).

6. 
$\underset{c}{(ClCH_2)_2}\overset{O}{\overset{\|}{P}}N(\underset{b}{CH_2}\underset{a}{CH_3})_2$ (VI). 27.2 g (0.15 mole) I with 21.9 g (0.3 mole) Et_2NH and 450 ml Et_2O as in 2 gives 17.8 g (54.5%) VI, m.p. 62.9–63.3° (from Et_2O) (Lit. [4] m.p. 64–5°). ^{31}P-34.2 ppm (in $CHCl_3$).

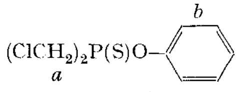
$C_6H_{14}Cl_2NOP$ (218.05) Calc. C 33.05 H 6.47 N 6.42% Found C 32.93 H 6.80 N 6.19%

7. 
$[(\underset{a}{CH_3}\underset{c}{CH_2}O)_2\overset{O}{\overset{\|}{P_\alpha}}\underset{b}{CH_2}]_2\overset{O}{\overset{\|}{P_\beta}}N(\underset{b}{CH_2}\underset{a}{CH_3})_2$ (VII). From 10.9 g (0.05 mole) VI and 33.2 g (0.2 mole) $(EtO)_3P$ at 160° [2]; 6.0 g (95%) EtCl were evolved. Distillation gave VII as a colorless oil b.p. 130–4°/0.01 Torr, $n_D^{20} = 1.4696$. The ^{1}H-NMR. as well as the ^{31}P-NMR. spectra indicate that in part Et_2N-groups were exchanged by EtO-groups: ^{31}P-chem. shifts −21.4 ppm (P_α) and −29.3 ppm (P_β); in addition there is a peak at −37.5 ppm arising from P_β of $[(EtO)_2P_\alpha(O)CH_2]_2P_\beta(O)OEt$ which is present. ^{1}H-NMR. (in $CDCl_3$): *a* at 1.33 ppm (*t*); *a'* at 1.14 ppm (*t*), *a* + *a'* 18 H; *b* at 2.78 ppm (broad, $J_{P_\alpha CH} = 18.5$, $J_{P_\beta CH}) = 20.3$ Hz, 3.76 H); *b'* at 3.15 ppm (2 *q*, $J_{HH} = 7$, $J_{PNCH} = 11$ Hz, 2.44 H), and *c* at 4.17 ppm (*m*, 9.64 H).

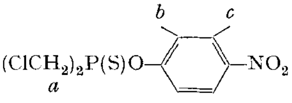


B. $\underset{a}{(ClCH_2)_2}\overset{S}{\overset{\|}{P}}Cl$ and Derivatives. – *8.* $\underset{a}{(ClCH_2)_2}P(S)Cl$ (VIII). A mixture of 181.3 g (1 mole) I and 50 g (0.22 mole) P_2S_5 is heated at 165° for 3 h. Distillation yields 148.3 g (75%) crude VIII which is shaken with ice water to remove I and then redistilled to give 118.5 g (60%) VIII, b.p. 46–8°/0.7 Torr, $n_D^{20} = 1.5897$, $d_4^{20} = 1.549$ (Lit. [5] b.p. 104–6°/10 Torr, $n_D^{20} = 1.5890$, $d_4^{20} = 1.5580$; [6] b.p. 92.5–3.5°/6 Torr, $n_D^{20} = 1.5872$, $d_4^{20} = 1.5483$). ^{31}P-chem. shift −81.9 ppm (subst.). ^{1}H-NMR. (in $CDCl_3$): shows non-equivalence of the H within the CH_2-groups but not two different CH_2-groups, *a* centered at 4.12 ppm ($J_{PCH} = 4.87$ Hz from ^{31}P-NMR.) (see Fig.).

$C_2H_4Cl_3PS$	Calc.	C 12.17	H 2.04	Cl 53.87	P 15.68	S 16.24%
(197.46)	Found	,, 12.27	,, 1.95	,, 53.47	,, 15.15	,, 17.46%

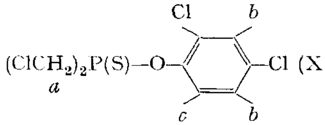
9. 

(IX). As in *2*, 3.94 g (0.02 mole) VIII, 1.88 g (0.02 mole) PhOH, 2.02 g Et_3N and 80 ml THF give 1.3 g (25.5%) IX, pale yellow crystals, m.p. 54.5–55° (from Et_2O/hexane) (Lit. [5] m.p. 56–57°).

10. 

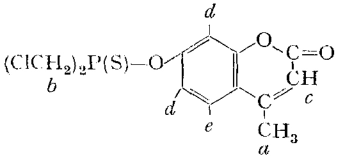
(X). As in *2*, 2 g (0.011 mole) VIII with 1.77 g (0.011 mole) p-$NO_2C_6H_4ONa$ and 100 ml acetone give 1.9 g (57.5%) X, pale yellow crystals, m.p. 76–76.3° (from $CHCl_3$/hexane).

$C_8H_8Cl_2NO_3PS$	Calc.	C 32.01	H 2.68	Cl 23.63	N 4.67%
(300.11)	Found	,, 31.95	,, 2.75	,, 23.48	,, 4.64%

11. 

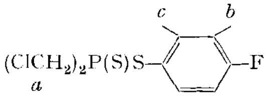
(XI). As in *2*, 4 g (0.022 mole) VIII with 3.6 g (0.022 mole) 2,4-$Cl_2C_6H_3OH$, 2.22 g Et_3N and 100 ml THF give 2.2 g (32.5%) XI, pale yellow crystals, m.p. 51.8–52.2° (from Et_2O/hexane).

$C_8H_7Cl_4OPS$ (324.0) Calc. C 29.66 H 2.18 Cl 43.78% Found C 29.68 H 2.28 Cl 43.64%

12. 

(XII). As in *2*, 2.0 g (0.011 mole) VIII with 2.18 g (0.011 mole) of Na salt of β-umbelliferon and 100 ml acetone give 1.7 g (48.1%) XII, m.p. 120–121° (from $CHCl_3$/hexane).

$C_{12}H_{11}Cl_2O_3PS$ (337.17) Calc. C 42.74 H 3.29 Cl 21.03% Found C 42.27 H 3.24 Cl 21.90%

13. 

(XIII). As in *2*, 3 g (0.015 mole) VIII, 1.9 g (0.015 mole) *p*-FC_6H_4OH, 1.5 g (0.015 mole) Et_3N and 70 ml acetone give XIII in white crystals, m.p. 50–50.5°.

$C_8H_8Cl_2FPS$ Calc. C 33.23 H 2.79 Cl 24.52 S 22.18%
(289.15) Found ,, 33.06 ,, 2.90 ,, 24.33 ,, 22.86%

14. $(\underset{c}{ClCH_2})_2P(S)N(\underset{b}{CH_2}\underset{a}{CH_3})_2$ (XIV). As in *2*, 3 g VIII, 2.22 g Et_2NH and 70 ml Et_2O give XIV as a liquid which crystallizes at – 20° (Lit. [5] b.p. 95°/10^-3^ Torr).

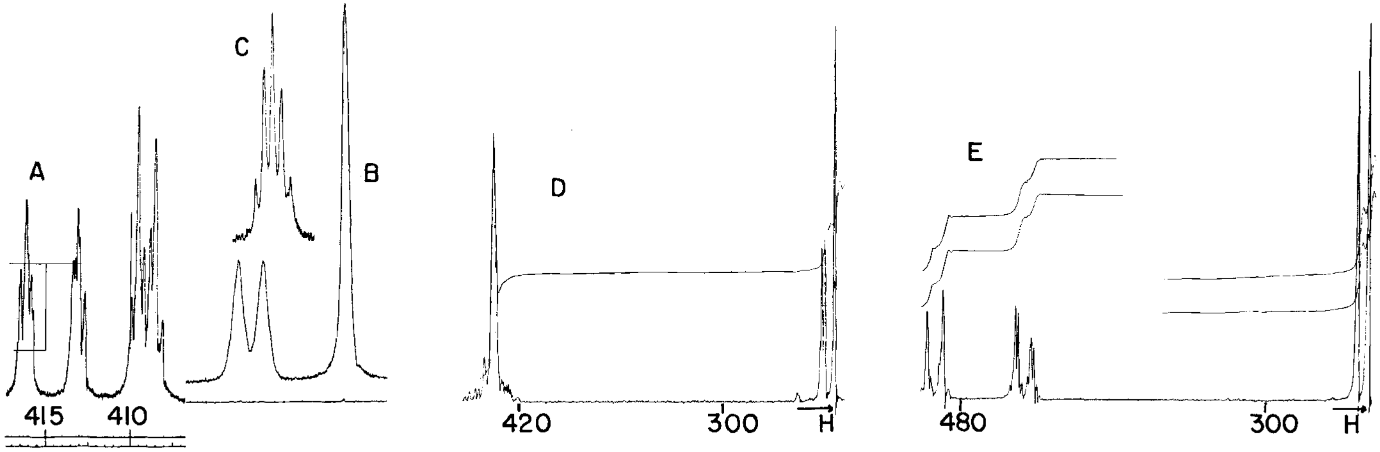
C. $(ClCH_2)_2PCl$ and Derivatives. – *15.* $(ClCH_2)_2PCl$ (XV). From 19.7 g (0.1 mole) VIII, and 34 g (0.11 mole) $(PhO)_3P$ at 170° [7]. Crude XV is continously distilled off at 100–110 Torr; redistillation of this crude XV (12.5 g; 75.7%) gives 10.1 g (61%) XV, colorless liquid, b.p. 45–47°/10 Torr, 68–70°/20 Torr (Lit. [6] b.p. 74–77°/16–18 Torr. [8] b.p. 76°/22 Torr). ^{31}P-chem.-shift – 71.9 ± 0.3 ppm (neat); ^1H-NMR. (in $CDCl_3$), 3.93 ppm (shows non equivalence of H within CH_2-groups.

16. $(\underset{b}{ClCH_2})_2P\underset{a}{CH_3}$ (XVI) and $(ClCH_2)_2CH_3PS$ (XVII). To 8.59 g (0.072 mole) of CH_3MgBr in 20 ml Et_2O 6.0 g (0.036 mole) XV in 20 ml Et_2O is added at – 20°. The temperature is then kept at – 5 to 0° for $^1/_2$ h, the mixture hydrolyzed with NH_4Cl-solution at 0° and the ether layer separated. Distillation of the ethereal solution gives 1.5 g (28.8%) XVI, a liquid, b.p. 44°/5 Torr. ^1H-NMR. (in $CD_3OD/CDCl_3$): *a* at 1.19 ppm (*d*, J_{PCH} = 3.6 Hz, 3 H), *b* at 3.72 ppm (*d*, J_{PCH} = 6 Hz, 4 H). The phosphine XVI is very sensitive towards oxygen and the ^1H-NMR. spectrum shows the presence of small amounts of oxide $(ClCH_2)_2P(O)CH_3$ with peaks for CH_3 at 1.76 (J_{PCH} = 13.3 Hz) and $ClCH_2$ 3.72 ppm (7 Hz) (Lit. [9] reports CH_3 at 1.74 ppm (J_{PCH} = 13.3 Hz) and $ClCH_2$ at 3.75 ppm (J_{PCH} = 7 Hz)).

0.5 g crude XVI in benzene is heated under reflux with sulfur during 5 h and benzene then evaporated. The residue dissolved in ether is filtered off from excess sulfur and Et_2O distilled off from the filtrate. The residue XVII is a yellow oil, spectroscopically pure: ^1H-NMR. (in $CDCl_3$), *a* at 1.91 ppm (J_{PCH} = 12.8 Hz, 3 H); and *b* at 3.84 ppm (J_{PCH} = 6 Hz, 4 H).

17. $(ClCH_2)_2PCH_2CH_3$ (XVIII), $(ClCH_2)_2(CH_3CH_2)P=S$ (XIX), and $(ClCH_2)_2(CH_3CH_2)P=O$ (XX). – *a*) XVIII is prepared as described in *16*, but MeMgBr replaced by EtMgBr. Distillation gives 1.5 g (23%) XVIII, b.p. 85°/20–22 Torr; the compound solidifies after some time and then shows a very complex ^1H-NMR. spectrum. Treatment of crude XVIII with sulfur in benzene solution (5 h heating under reflux) gives the sulfide XIX, white crystals, m.p. 30.5–31° (from Et_2O/hexane).

$C_4H_9Cl_2PS$ Calc. C 25.14 H 4.75 Cl 37.14 S 16.78%
(191.06) Found ,, 25.03 ,, 4.83 ,, 37.18 ,, 17.99%

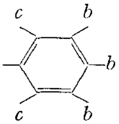


Resonance spectra of derivatives of bis-chloromethyl-thiophosphinic acid

A) ^{1}H-NMR. spectrum of $(ClCH_2)_2P(S)Cl$ in $CDCl_3$ at 100 MHz; B) As for A but at 60 MHz; C) ^{31}P-NMR. spectrum of $(ClCH_2)_2P(S)Cl$ in $CHCl_3$; D) ^{1}H-NMR. spectrum of $(ClCH_2)_2P(S)OC_6H_5$in $CDCl_3$; E) ^{1}H-NMR. spectrum of $(ClCH_2)_2P(S)OC_6H_4NO_2$-*p* in $CDCl_3$

b) As an alternative, 10 g (0.06 mole) XV, 16 g (0.12 mole) EtMgBr$_2$, and 100 ml Et$_2$O is treated at 0° with bromide dissolved in H$_2$O, NaHCO$_3$ added, the mixture filtered, and the ether layer separated. As evaporation of the ethereal solution gives only 0.3 g XX, the aqueous layer is evaporated to dryness and the residue twice extracted with 250 ml CHCl$_3$. Distillation of the combined CHCl$_3$ extracts gives 8.2 g (77.6%) XX, b.p. 91–92°/0.5 Torr, which solidifies at room temperature, m.p. 42.5–43° (Lit. [9] b.p. 91–93°/0.5 Torr, m.p. 42–44°). The ^{31}P- and ^{1}H-NMR. spectra agreed with those of an authentic sample [9].

18. (ClCH$_2$)$_2$P(S)—



(XXI). The crude reaction mixture from 6 g (0.036 mole) XV and 15.05 g (0.072 mole) PhMgBr in 50 ml Et$_2$O was hydrolyzed with NH$_4$Cl-solution, the Et$_2$O-phase separated, and ether distilled off. The residue was taken up in benzene, sulfur added, heated under reflux for 5 h, the benzene evaporated, and the product several times recrystallized from Et$_2$O/hexane. Crystalline XXI was obtained m.p. 41–41.5°.

$C_8H_9Cl_2PS$ (239.1) Calc. C 40.18 H 3.79% Found C 40.09 H 3.75%

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177. Equilibres conformationnels de glucides au niveau de liaisons σ sp^2-sp^3 C-C. II[1])

Dérivés d'hydrazones d'*aldéhydo*-sucres

par **J. M. J. Tronchet, Br. Baehler, A. Jotterand**[2]) et **M^lle F. Perret**
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(25 VI 71)

Summary. A series of alkyl- and aryl-hydrazones of different types of *aldehydo*-sugars with blocked hydroxy groups have been studied, mainly by PMR. spectroscopy. No traces of the azo-alkane or ene-hydrazine forms were detected; the hydrazones were found to exist only in the *syn*

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[1]) La référence [1] constitue la première communication de cette série.

[2]) Les composés de configuration *arabino* ont fait l'objet de la thèse de Doctorat ès Sciences [2] de cet auteur.