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SILICON-PHOSPHORUS ANALOGIES. NUCLEOPHILIC CATALYSIS IN THE ALCOHOLYSIS OF CHLOROPHOSPHORUS DERIVATIVES

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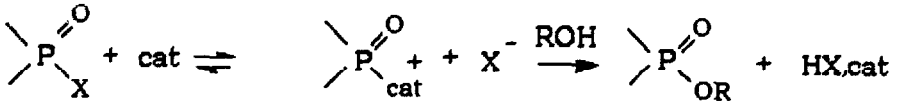
Abstract

The mechanism of the alcoholysis of chlorophosphonates and chlorophosphates in the presence of nucleophilic catalysts like hexamethylphosphotriamide, pyridine and N-methylimidazole is discussed on the basis of kinetic and stereochemical results.We have proposed a mechanism for the reaction , which is governed by entropy , involving reaction of the alcohol with a pentacoordinated intermediate . This accounts for the differences in the stereochemical outcome and the rate equation which can be derived for the reaction with a variety of substrates in addition to the absence of common ion + solvent effects observed.

INTRODUCTION

The mechanism of the nucleophilic catalysis of the nucleophilic substitution at phosphorus is commonly interpreted by two consecutive $SN_2(P)$ reactions [1,2] (Scheme 1).

Scheme 1



A

The leaving group X is substituted by the nucleophilic catalyst (cat) leading to a very reactive intermediate. The nucleophile then reacts with this intermediate giving the product.

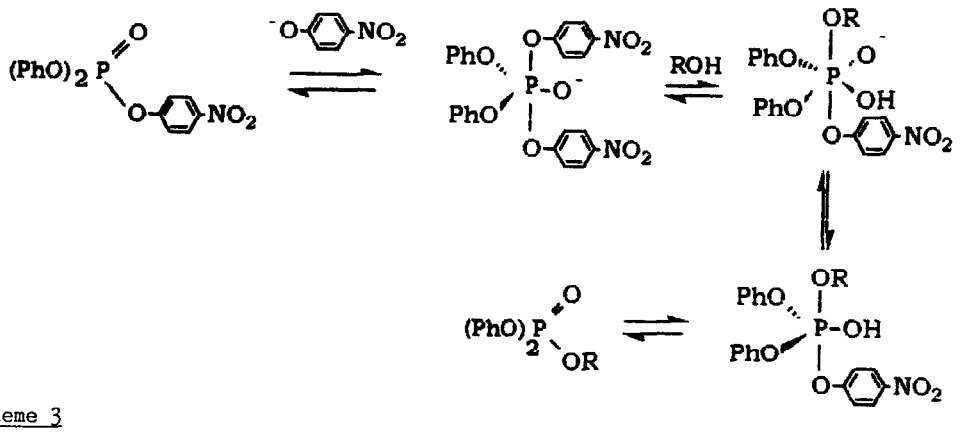
Evidence for this mechanism has been demonstrated by the decrease of the rate of reaction when a common ion is added [3] or by a kinetic study of the synthetized intermediate when possible [3,4].

Nevertheless, this mechanism does not explain the catalysed substitutions where the catalyst is the same as the leaving group. Thus, the formation of hypervalent intermediates during the alcoholysis of 4-nitrophenyldiphenylphosphate catalysed by 4-nitrophenate anion has been postulated by Ramirez [5] (Scheme 2).

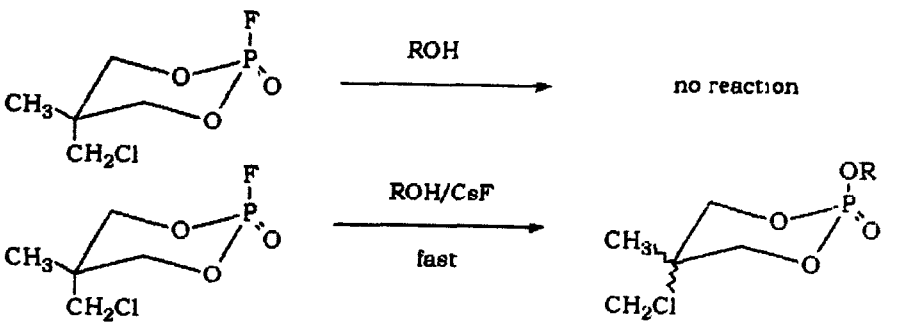
In the same way, the fluoride activation of nucleophilic substitution of fluoro-

phosphates offers another example of the participation of external nucleophiles in $SN_2(P)$ reactions [6] (Scheme 3).

Scheme 2

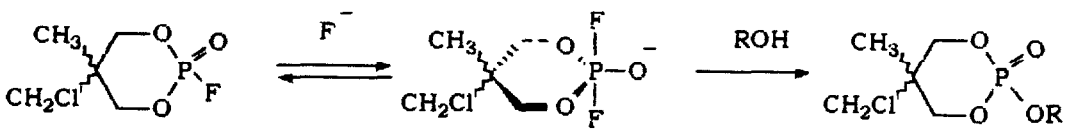


Scheme 3



The fluorophosphate does not react with alcohol alone ; however, in the presence of fluoride ions, the alcoholysis is a very fast reaction giving a kinetic ratio of diastereoisomeric products close to 55/45 which is independent of the nature of ROH. This result was interpreted in terms of the formation of a pentacoordinated phosphorus which reacts with the alcohol (Scheme 4).

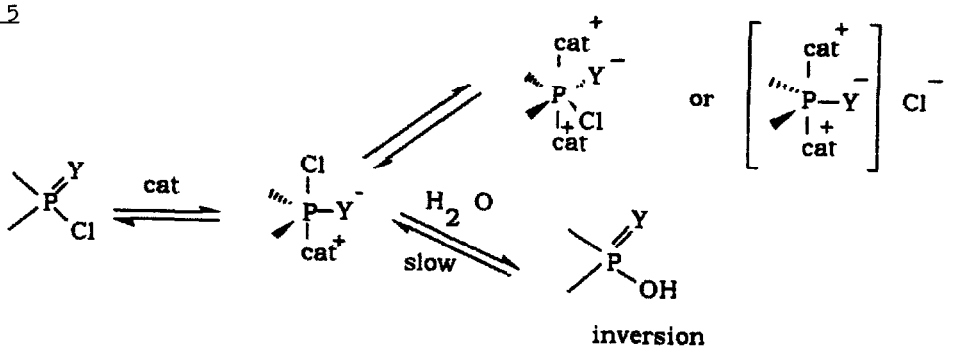
Scheme 4



We have also reported a strong analogy between chlorosilanes and chlorophosphonates in the mechanism of racemization and hydrolysis catalysed by nucleophilic agents [7]. This also involves the formation of a pentacoordinated intermediate (Scheme 5).

In order to determine whether the nucleophilic catalysis involves the formation of a pentacoordinated intermediate, we have investigated the alcoholysis of chlorophosphates and chlorophosphonates in the presence of nucleophilic activating agents like hexamethylphosphotriamide (HMPA), pyridine (Py) and N-methylimidazole (NmI).

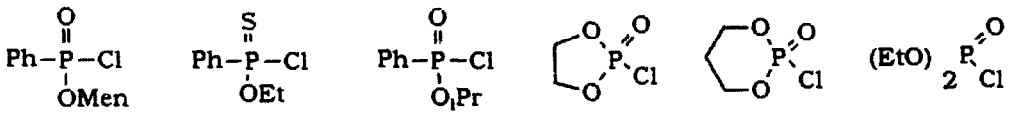
Scheme 5



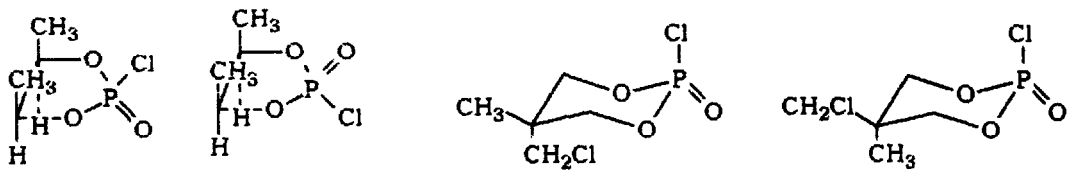
Results

The starting materials used are the following :

O-menthylchloro(phenyl)phosphonate 1, O-Ethylchloro(phenyl)thio-phosphonate 2, O-ipropylchloro(phenyl)phosphonate 3, 2-chloro-2-oxo-1,3,2 dioxaphospholane 4, 2-chloro-2-oxo-1,3,2 dioxaphosphorinane 5, chlorodiethylphosphate 6, 4,5-dimethyl-2-chloro-2-oxo-1,3,2 dioxaphospholane 7 and 2-chloro-5-chloromethyl-5-methyl-2-oxo-1,3,2 dioxaphosphorinane 8.



1 2 3 4 5 6

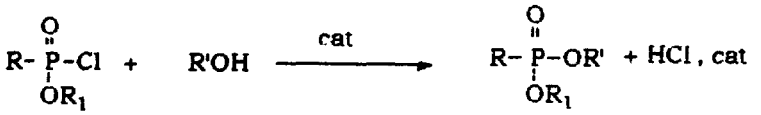


7 cis 7 trans 8 cis 8 trans

As previously reported, chlorophosphonates do not react with HMPA or NmI alone [7], whereas chlorophosphates react with NmI or HMPA giving betaïnes [8]. These species have never been detected when the mixture of alcohol and catalyst was added to the chlorophosphates and only the substitution of Cl by the alcohol was observed (Scheme 6).

The nucleophilic activating agents (cat) are consumed in the reaction, but they are true catalysts when the reaction is performed in presence of Et_3N, a more basic amine. So we will call them unproperly catalysts throughout this paper.

Scheme 6



R=alkyl or alkoxyl

Kinetics

The rate laws and the corresponding rate constant values as well as the results of the hydrolysis of chlorophosphonates **1** and **2** [7] are listed in table 1.

The alcoholysis, without catalyst, of chlorophosphates and chlorophosphonates is first order with respect to both the chlorophosphorus derivative and the alcohol [9].

$$r = k\,[P]\,[ROH]$$

Three kinds of rate laws are evidenced in presence of catalysts.

- Second order reaction : $r = k\,[P][cat]$

The rate law is first order with respect to the phosphorus derivative and to the catalyst and does not depend on the alcohol concentration.

This law is typical of the catalysis by NmI in CH_2Cl_2 regardless of the phosphorus species and the alcohol but it does not hold true in acetonitrile.

- Third order reaction : $r = k\,[P]\,[cat][ROH]$

The reaction is first order with respect to the phosphorus species, the catalyst and the nucleophile.

This rate law was found for the slower reactions e.g. the hydrolysis of chlorophosphonates in presence of DMF, DMA and HMPA in CCl_4 [7].

- "Complex" order reaction : $r = \dfrac{k\,[P][cat][ROH]}{1 + k'[ROH]}$

The reaction is neither second or third order and the rate slows down with increasing alcohol concentration.

This rate law is observed with HMPA and Py as catalysts in CH_2Cl_2 and NmI in CH_3CN.

Table 1 - Rate orders and rate constants

Reactants	ROH	Cat/Solvent	Rate order	Rate constants (0°C)
1	EtOH	NmI/CH_2Cl_2	2nd order[a]	$k = 1.15\ l.mol^{-1}s^{-1}$
	MeOH	HMPA/CH_2Cl_2	complex order	$k = 4.3x10^{-3}l^2mol^{-2}s^{-1}$ $k' = 3\ l.mol^{-1}$
	H_2O	DMA/CCl_4	3rd order[c]	$k = 1.45x10^{-3}l^2mol^{-2}$
	H_2O	DMF/CCl_4	3rd order[c]	$k = 2.76x10^{-3}l^2mol^{-2}s^{-1}$
	H_2O	HMPA/CCl_4	3rd order[c]	$k = 10.6x10^{-3}l^2mol^{-2}s^{-1}$
2	H_2O	DMF/CCl_4	3rd order	$k = 7.2x10^{-5}l^2mol^{-2}s^{-1}$
3	EtOH	CH_2Cl_2	2nd order[b]	$k = 2.3x10^{-4}.mole^{-1}s^{-1}$
	MeOH	NmI/CH_2Cl_2	2nd order[a]	$k = 6.0\ l.mol^{-1}s^{-1}$
	MeOH	HMPA/CH_2Cl_2	complex order	$k = 2.3 \times 10^{-2}l^2mol^{-2}s^{-1}$ $k' = 7\ l.mol^{-1}$
4	EtOH	CH_2Cl_2	2nd order[b]	$k = 0.011\ l\ mol^{-1}s^{-1}$
	EtOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.3\ l\ mol^{-1}s^{-1}$
	MeOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.19\ l\ mol^{1}s^{-1}$
	MeOH	NmI/Et_3N/CH_2Cl_2	2nd order[a]	$k = 0.16\ l\ mol^{-1}s^{-1}$
	PhOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.08\ l\ mol^{-1}s^{-1}$
	H_2O	NmI/CH_3CN	2nd order[a]	$k = 0.24\ l\ mol^{-1}s^{-1}$
5	EtOH	CH_2Cl_2	2nd order[b]	$k = 3.8\ x10^{-7}l\ mol^{-1}s^{-1}$
	EtOH	NmI/CH_2Cl_2	2nd order[a]	$k = 4.5 \times 10^{-2}l\ mol^{-1}s^{-1}$
6	EtOH	CH_2Cl_2	2nd order[b]	$k = 1.4 \times 10^{-6}l\ mol^{-1}s^{-1}$
	EtOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.10\ l\ mol^{-1}s^{-1}$
	EtOH	Pyridine/CH_2Cl_2	complex order	$k = 8.9 \times 10^{-2}l^2mol^{-2}s^{-1}$ $k' = 15\ l\ mol^{-1}$
	EtOH	HMPA/CH_2Cl_2	complex order	$k = 4.4 \times 10^{-4}l^2mol^{-2}s^{-1}$ $k' = 20\ l\ mol^{-1}$
	EtOH	NmI/CH_3CN	complex order	$k = 23.6\ l^2mol^{-2}s^{-1}$ $k' = 35\ l\ mol{-}1$
	MeOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.16\ l\ mol^{-1}s^{-1}$
	PhOH	NmI/CH_2Cl_2	2nd order[a]	$k = 0.06\ l\ mol^{-1}s^{-1}$

a) $r = k\,[P]\,[NmI]$ b) $r = k\,[P]\,[ROH]$ c) 25°C

Activation parameters

The activation parameters for each kind of rate law are summarized in table 2.

Whatever the rate law, the activation parameters found are more or less the same. The activation energy is low and the activation entropy is high.

Table 2 - Activation parameters

Reactant	ROH	Cat	Rate law	ΔE_a a)	ΔH^* a)	ΔG a)	ΔS^* b)
$(EtO)_2P(O)Cl$	EtOH	NmI	$r = k[P][NmI]$	4.9	4.3	18	-47
Ph(OiPr)P(O)Cl	MeOH	HMPA	$r = \frac{k[P][HMPA][ROH]}{1 + k'[ROH]}$	7.5	6.9	19	-40
Ph(OMen)P(O)Cl	H_2O	DMF	$r = k[P][DMF][H_2O]$	7.3	6.7	21	-48
"	"	DMA	"	5.0	4.4	21	-56

a) kcal.mole^{-1} b) cal.°K^{-1}mole^{-1}

Solvent effects

The rate law is modified when the more polar solvent CH_3CN is used instead of CH_2Cl_2 for the ethanolysis of diethylchlorophosphate **6** catalysed by NmI (Table 1). Nevertheless the half life of the reaction is only slightly affected ($t_{1/2}$ 100s in CH_2Cl_2 v.s. 30s in CH_3CN).

Common ion effects

The half lives of the alcoholysis of different reactants with and without added salts, are summarized in table 3.

The presence of Cl^- anions does not dramatically change the half lives of the reactions. The small increase in the rate of reaction in presence of Cl^- is of the same order as that with ClO_4^- and is probably due to the increase in the ionic strength of the medium.

Stereochemistry

The stereochemistry of the catalysed alcoholysis was investigated using the optically active chlorophosphonate 1(S)p, the mixtures of the isomeric chlorophosphates **7** cis and trans and **8** cis and trans.

The configurations were assigned on the basis of ^{1}H and/or ^{31}P NMR spectra as previously reported [10].

The results are summarized in table 4.

Table 3: Half lives of catalysed alcoholysis with added salts at 0°C

Reactant	[PCl]	[ROH]	[cat]	$[R_4N^+X^-]$	t 1/2
6 2nd order	0.01	0.01	0.01	0	16 min a)
	0.01	0.01	0.01	0.01	12 min a)
	0.1	0.1	0.1	0	100 s. a)
	0.1	0.1	0.1	0.2	45 s. a)
	0.1	0.1	0.1	0.12	51 s. b)
	0.1	0.1	0.1	0.1	40 s. c)
8 "complex order"	0.1	2.47	2.28	0	4h15 d)
	0.1	2.47	2.28	0.18	4h15 d)
	0.1	4.94	1.14	0	27h e)
	0.1	4.94	1.14	0.126	21h e)
1 "complex order"	0.1	0.1	0.1	0	6h30 f)
	0.1	0.1	0.1	0.34	4h30 f)

a) ROH = EtOH, cat = NmI, $R_4N^+X^-$ = $Et_4N^+Cl^-$, solvent CH_2Cl_2

b) ROH = EtOH, cat = NmI, $R_4N^+X^-$ = $nBu_4N^+Cl^-$, solvent CH_2Cl_2

c) ROH = EtOH, cat = NmI, $R_4N^+X^-$ = $nBu_4N^+ClO_4^-$, solvent CH_2Cl_2

d) ROH = MeOH, cat = HMPA, $R_4N^+X^-$ = $nBu_4N^+Cl^-$, solvent CH_2Cl_2

e) ROH = MeOH, cat = HMPA, R_4NX = $nBu_4N^+Cl^-$, solvent CH_3CN

f) ROH = MeOH, cat = HMPA, R_4NX = nBu_4NCl^-, solvent CH_2Cl_2.

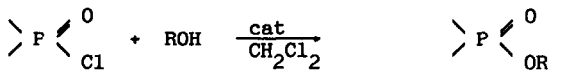
Methanolysis of 1(S)p without catalyst occurs with inversion. The percentage of inversion decreases in the presence of DMF or HMPA (85-89 %) although 1 is not epimerized during the reaction process. However with NmI or Py as catalysts, the methanolysis gives the thermodynamic mixture. This is due to the rate of epimerisation which is greater than the rate of alcoholysis [7].

Full retention at phosphorus is obtained in the alcoholysis of 7 regardless of the catalyst used and the isomeric ratio. The direct alcoholysis of 8 is a very slow and highly stereoselective reaction with inversion at phosphorus [11]. On the other hand alcoholysis of 8

in presence of NmI, HMPA or Py leads predominantly to retention at phosphorus.

Table 4

Stereochemical data of the catalysed alcoholysis of 1, 7, 8 in CH_2Cl_2



Reactant		ROH	Catalyst	Product	
1 $(S)_P$	$(R)_P$			% $(R)_P$ (RN)	% $(S)_P$ (IN)
100	0	MeOH	Without	6	94
		"	DMF	15	85
		"	HMPA	11	89
		"	Py	40	60
		"	NmI	39	61
		"	0.5% NmI*	39	61
60	40	"	NmI	41	59
7 Cis	Trans			% cis	% trans
18	82	MeOH	NmI	18	82
"	"	"	Py.	25	75
"	"	"	Py (solvent)	25	75
60	40	"	NmI	58	42
"	"	"	Py	54	46
22	78	EtOH	NmI	25	75
"	"	PhOH	"	24	76
15	85	MeOH	Without*	18	82
72	28	"	Without*	71	29
8 Cis	Trans			% cis	% trans
98	2	MeOH	NmI	77	23
"	"	MeOH	0.5 NmI	77	23
"	"	"	HMPA	97	3
"	"	EtOH	NmI	78	22
"	"	"	HMPA	98	2
"	"	pMeΦOH	Py	70	30
"	"	"	NmI	92	8

* with 1 equivalent Et_3N

DISCUSSION

Before discussing the mechanism of the nucleophilic catalysis, it is worth examining the efficiency of different catalysts in the ethanolysis of chlorophosphorus species (Table 5).

Table 5 - Half lives of the ethanolysis of diethylchlorophosphate 6 - [6] = 0.1N [EtOH] = 0.1N [cat] = 0.1N in CH_2Cl_2 at 0°C.

Cat	t 1/2 s.	$\frac{\text{t 1/2 without}}{\text{t 1/2 cat.}}$
without	7×10^6	1
HMPA	5×10^5	1.4×10^1
Py	3×10^3_2	2.3×10^3_4
NmI	1×10	7×10

The order of efficiency of the catalysts is as follows :

NmI > Py > HMPA > without

The dramatic effect of NmI is emphasized in table 6.

Table 6 - Rate constants of the ethanolysis of chlorophosphorus species with and without NmI in CH_2Cl_2 at 0°C ($l.mole^{-1}\ s^{-1}$)

Compound	k_1 a)	k_2 b)	k_2/k_1
3	2.3×10^{-4}	6	2.6×10^4
4	1.1×10^{-2}	0.3	2.7×10^1
5	3.8×10^{-7}	4.5×10^{-2}	1.2×10^5
6	1.4×10^{-6}	0.1	7.1×10^4

a) $r = k_1$ [P][EtOH] (without NmI) b) $r = k_2$ [P][NmI]

NmI is a very effective catalyst for the alcoholysis of the chlorophosphonate 3 and

chlorophosphates 5 and 6

$$(2 \times 10^4 < \frac{kNmI}{k \text{ without}} < 1 \times 10^5).$$

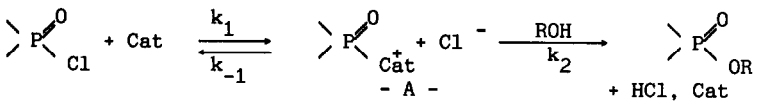
The five membered ring chlorophosphate 4 is very reactive towards nucleophilic substitution reactions due to its strained structure [10], and addition of NmI does not change dramatically the rate of the reaction.

Let us now discuss the two interpretations of the nucleophilic catalysis.

1°) Double displacement process

The mechanism is shown in scheme 7 :

Scheme 7



This mechanism is characterised by two consecutive SN_2 reactions. In most cases phosphates and phosphonates react with inversion [12], except for the exocyclic substitution of five-membered ring systems which leads to retention [10,13]. The overall stereochemical outcome would be retention due to two consecutive inversions (or two consecutive retentions for the compound 7).

The retention observed for the alcoholysis of chlorophosphates 7 and 8 catalysed by HMPA, NmI and Py agrees with this mechanism, but the inversion observed for the methanolysis of chlorophosphonate 1 or the hydrolysis of 2 does not. This overall stereochemical outcome would imply one step proceeding with retention, a result which has never been reported for SN_2 reactions of phosphono derivatives.

Furthermore, this mechanism involves the formation of an ionic intermediate A. Hence, the rate of the ethanolysis of 6 should have been more than three times that experimentaly observed, on using a more polar solvent.

In the same way, addition of a common ion, Cl^-, should have slowed down the overall reaction by increasing the rate of the reverse reaction [3] .However, regardless of the systeme used or the difference in rate orders, addition of Cl^- anions did not decrease the rate of the reactions but rather a small increase was observed.

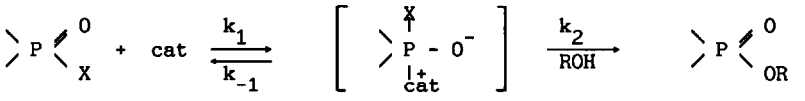
Therefore it seems reasonable to assume that A is not the intermediate in the nucleophilic catalysed alcoholysis of chlorophosphorus species.

2°) Mechanism involving a pentacoordinated intermediate

The first step is the equilibrated formation of a trigonal bipyramidal intermediate B by apical coordination of the catalyst to the phosphorus atom opposite the chlorine atom. The alcohol then attacks this reactive intermediate giving the product.

This mechanism which was proposed earlier [7] is reported in scheme 8.

Scheme 8



- B -

The kinetic treatment of this scheme using the Bodenstein steady state approximation leads to the following equation :

$$-\frac{d[P]}{dt} = \frac{\frac{k_1 k_2}{k_{-1}}\,[P]\,[Cat]\,[ROH]}{1 + \frac{k_2}{k_{-1}}\,[ROH]}$$

This rate law is identical to the "complex" order observed experimentally assuming $k = k_1k_2 / k_{-1}$ and $k' = k_2 / k_{-1}$.

This rate law simplifies in the limiting cases :

if $\frac{k_2}{k_{-1}} << 1$ $\quad r = k_1 \frac{k_2}{k_{-1}} [P]\,[Cat]\,[ROH]$ 3rd order

if $\frac{k_2}{k_{-1}} >> 1$ $\quad r = k_1\,[P]\,[Cat]$ 2nd order

which are the two other rate laws experimentally observed.

It can be noted that the second order reaction is only observed with the more efficient catalyst (NmI), in which case the rate determining step is the coordination of NmI to the phosphorus derivative.

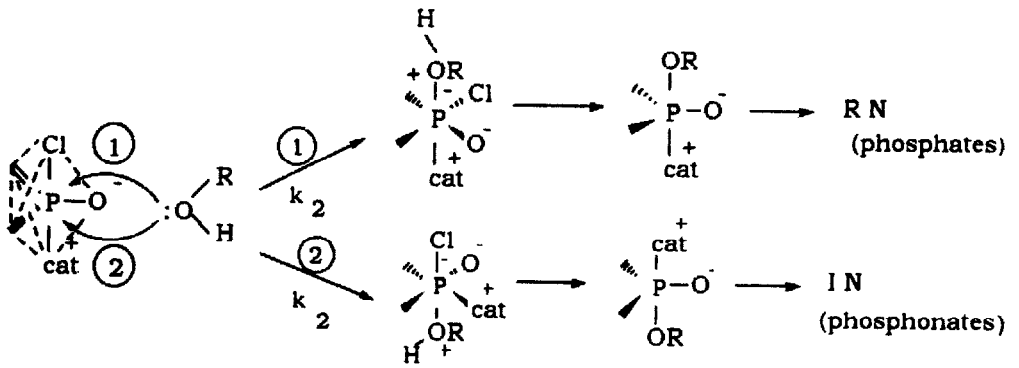
The third order reaction is observed with the less effective catalysts : DMF, DMA, HMPA, in the special case of hydrolysis in CCl_4. The rate determining step is the attack of H_2O on the intermediate B.

Catalysis by Py and HMPA in CH_2Cl_2 or NmI in CH_3CN leads to "complex" order reaction.

The proposed mechanism accounts for all the experimental facts ie :

- 1) The different rate laws.
- 2) The activation parameters which remain of the same magnitude corresponding to a process controlled by entropy ($4,9 < Ea < 7$ kcal.mole^{-1}, $-40 < \Delta S^{\neq} < -56$ u.e).
- 3) The absence of common ions and solvent effects. The stereochemistry can be interpreted, as previously proposed [7], by different geometries of nucleophilic attacks on the pentavalent intermediate B (Scheme 9).

Scheme 9

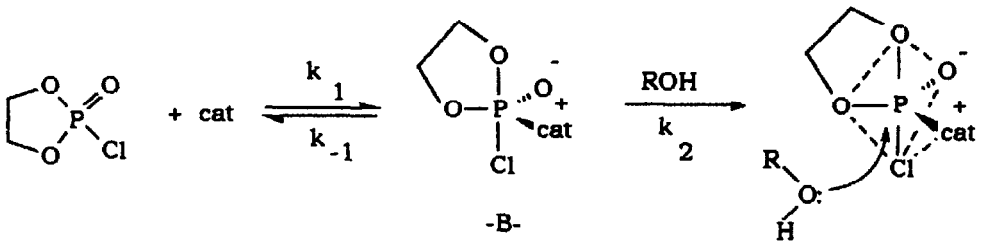


The retention of configuration observed with chlorophosphates corresponds to attack by path (1) (ClPOR < 90°C) similar to the nucleophilic catalysed hydrolysis of chlorosilanes [15]. Attack by the second pathway (2) accounts for the inversion observed on chlorophosphonates (ClPNu > 90°) [7]. Approach of the nucleophile in the plane defined by the phosphoryl oxygen and the two other substituents would give epimerisation [7].

In the case of the five membered-ring compound 4, we can assume the formation of the intermediate (B) by frontal attack of the catalyst on the P atom in line with our previous results on the nucleophilic substitution of this compound [10]

The overall retention observed corresponds, again, to a ClPOR < 90° approach of the nucleophile.

Scheme 10



Nevertheless this mechanism implies that the pentacoordinated intermediate is much more reactive than the tetracoordinate starting material. This point was the subject of conflicting mechanistic views in organosilicon chemistry [16]. Indeed the silicon center of the pentacoordinated adduct should be both more sterically hindered and less electrophilic than the tetracoordinated one and so less susceptible to nucleophilic attack. But recent work on the nucleophilic substitution of hypervalent silicon species [17-20] emphasizes their unusual reactivity, demonstrating that these criteria of steric hindrance or reduced electrophilicity cannot be schematically extrapolated from standard organic chemistry.

CONCLUSION

NmI is a very efficient catalyst for the alcoholysis of chlorophosphorus derivatives.

The kinetic results on the nucleophilic catalysed alcoholysis of chlorophosphorus species : i.e. three different rate laws involving the same activation parameters, and the absence of common ion and solvent effects, are betterinterpreted by the mechanism involving the formation of a pentacoordinated species followed by the attack of the alcohol on this intermediate. The rate determining step is strongly dependent on the catalyst used.

The stereochemistry depends on the substrate, chlorophosphonates react with inversion and chlorophosphates with retention.

The mechanism of the nucleophilic catalysed alcoholysis is the same for both chlorophosphorus and chlorosilicon species.

EXPERIMENTAL SECTION

Reactions were carried out in Schlenk tubes under dry N_2. ^1H NMR spectra were recorded on a Varian EM 390 apparatus, with TMS as internal reference. ^{31}P NMR spectra were measured at 32.37 MHz on a Fourier Transform Bruker WP 80. Positive chemical shifts are downfield relative to external 85 % H_3PO_4 diluted in D_2O (lock signal). IR spectra were obtained with a Perkin-Elmer 298.

- Preparation

Most compounds were prepared as described elsewhere : menthylchloro(phenyl)-phosphonate 1 [7], 2-chloro-2-oxo-1,3,2 dioxaphospholane 4 [21, 22], 2-chloro-2-oxo-1,3,2-dioxaphosphorinane 5 [19,20], diethylchlorophosphate 6 [23], 2-chloro-5-chloromethyl-5-methyl-2-oxo-1,3,2 dioxaphosphorinane 8 [24] and 2-chloro-4-5 dimethyl-2-oxo-1,3,2 dioxaphospholane 7 [10].

The isopropylchloro(phenyl)phosphonate 3 was prepared as follow :

Dichlorophenylphosphine (65.95g, 0.368 mole) was added dropwise at 0°C to isopropanol (150 ml, 1.95 mole) under N_2. After stirring for 12 hours, the isopropanol was evaporated and the residue distilled yielding i-propyl(phenyl)phosphonate (61.74g, 0.335 mole) bp 0.05 = 110-120°C. ν_{P-H} = 2350 cm^{-1}, $\nu_{P=O}$ = 1240 cm^{-1}, $\delta_H(CDCl_3)$ 1.4 and 1.3 ppm ;(d, 6H) 4.65 ppm (m, 1H) 7.48 ppm (d, 1H J_{P-H} = 561.6 Hz) 7.6 ppm (m, 5H).

Cl_2 was passed though the solution of i-propyl(phenyl)phosphonate (0.335 mole) in CCl_4 (250 ml) at 0°C. After evaporation of CCl_4 and distillation 52.44 g (0.24 mole) of i-propylchloro(phenyl)phosphonate 7 was obtained. b.p. = 104°C, $\nu_{P=O}$ = 1240 cm^{-1}, ν_{P-OR} = 980 cm^{-1} ;$\delta_H(CDCl_3)$ = 1.21 and 1.25 ppm (d, 6H) 5 ppm (m, 1H) 7.7 ppm (m, 5H) $\delta_P(CH_2Cl_2)$ + 25.2 ppm. - Anal. calculated for $C_9H_{12}ClO_2P$: C, 49.42 ; H, 5.49 ; Cl, 16.2 ; P, 14.18 ; found C, 48.80 ; H, 5.44 ; Cl, 15.86 ; P, 14.41.

Most of the products of the reaction of the starting materials with alcohols have already been described [7,10].

Methyl i-propyl(phenyl)phosphonate :

A mixture of methanol (0.04 g, 1.25 mmole) and triethylamine (0.127 g, 1.25 mmole) in CH_2Cl_2 (5ml) was added to a solution of i-propyl(phenyl)phosphonate (0.25 g, 1.25 mmole) in CH_2Cl_2 (5 ml). After stirring for 1 hour, CH_2Cl_2 was evaporated in vacuo, benzene was added and triethylammonium chloride was filtered off. Evaporation of the solvent yielded methyl i-propyl(phenyl)phosphonate (0.27 g, 0.17 mmole), $\delta_H(CDCl_3)$ 1.23 and 1.38 ppm (d, 6H) 3.63 ppm (d, 3H) 4.67 ppm (m, 1H) 7.43 ppm (m, 5H), $\delta_P(CH_2Cl_2)$ + 18.05 ppm.

- Reaction of catalysts with chlorophosphorus derivatives

The characterisation of the products was determined by means of proton decoupled ^{31}P Fourier transform NMR Spectroscopy. 1 mmole of the chlorophosphorus derivative was diluted in 2 ml of dichloromethane in the NMR tube, 1 mmole of catalyst was then added and the spectrum recorded.

Addition of catalysts to the chlorophosphonates does not change the spectra.

1°/ Addition of NmI to 2-chloro-2-oxo-1,3,2 dioxaphospholane 4

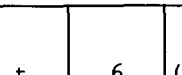
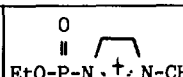
The signal at δ_P = 22.2 ppm corresponding to 4 can never be observed and a single new signal appears at δ_P = - 11.4 ppm. The product was isolated in another experiment. A solution of NmI (7.25 mmoles) in benzene 15 ml was added dropwise to a solution of 4 in benzene (15 ml) under nitrogen. Precipitation occurred, filtration gave a hygroscopic product. mp = 110°C, δ_H (CD_2Cl_2) 3.73 ppm (t, 2H) 4.0 (m, 2H) 4.0 (s, 2H) 7.5ppm (s, 2H) 9.4 ppm (s, 1H).
- Anal. calc. for $C_6H_{10}ClN_2O_3P$: C, 32.07 ; H, 4.45 ; Cl, 15.81 ; P, 13.8 ; N, 12.47 found C, 32.17 ; H, 4.61 ; Cl, 15.79 ; P, 12.45; N, 12.40.

2°/ Addition of NmI to diethylchlorophosphate 6

The addition of NmI to 6 (δ_P = + 3.6 ppm) leads to 3 products (δ_P = - 9.9 ppm , δ_P = - 10.5 ppm and δ_P = - 13.3 ppm).

The percentage of product versus time is reported in table 7.

Table 7

t	6 + 3.6	 - 9.9 ppm	 -10.5ppm	 - 13.3ppm
3mm	50 %	28.6 %	21.3 %	0 %
15mm	33 %	12.7 %	35.9 %	18.4 %
2h	0 %	0	69 %	31 %

- 3°/ Addition of pyridine to 6

Only the slow formation of polyphosphates is observed.

- 4°/ Addition of HMPA to 4

Two doublets at δ_P = - 10.2 ppm and δ_P = + 26.4 ppm appear slowly.

- 5°/ Addition of HMPA to 6

The formation of two doublets at δ_P = - 10.1 ppm and δ_P + 26.4 ppm is very slow (6 % in 3h30). Pyrophosphate (δ_P = - 13.3 ppm) is also formed slowly.

- Kinetics

All solvents were purified before use. CH_2Cl_2 was distilled over P_2O_5, CH_3CN over P_2O_5 (three times), CH_3OH and C_2H_5OH over magnesium methoxide and ethoxide respectively.

HMPA was first distilled over Na and then redistilled over CaH_2 ; pyridine and N-methylimidazole over KOH pellets.

The concentration of water was measured by titration with Karl Fisher's reagent.

Methods

The general method has been described in a previous paper [10].

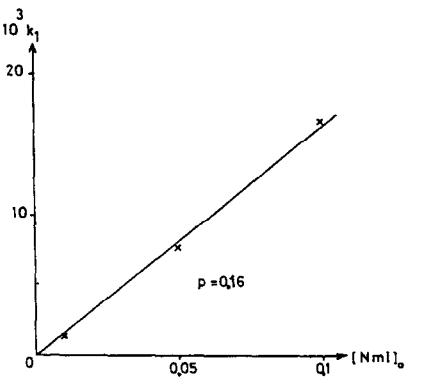
Catalytic effect of NmI in the presence of Et_3N

The first order of the methanolysis of diethylchlorophosphate in the presence of Et_3N as an acceptor of HCl vs the concentration of the catalyst NmI is reported in table 8 and figure 1.

Table 8

$(EtO)_2P(O)Cl$ mole l^{-1}	MeOH mole l^{-1}	NmI mole l^{-1}	Et_3N mole l^{-1}	k_{s-1}
0.1	0.1	0.01	0.1	1.39×10^{-3}
0.1	0.1	0.05	0.1	7.70×10^{-3}
0.1	0.1	0.10	0.1	16.66×10^{-3}

Figure 1 : First order vs [NmI]



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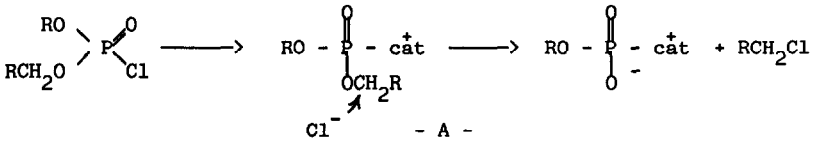
14. The formation of betaine, without alcohol, is interpreted by the formation of the intermediate A followed by the attack of Cl^- anion on the carbon atom leading to betaine and chloroalkane (Scheme 11).

Scheme 11



The addition of Cl^- should accelerate the formation of the betaïne. However, this species is never observed in the catalysed alcoholysis of chlorophosphates even in presence of added Cl^-.

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