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REEXAMINATION OF THE FRIEDEL-CRAFTS REACTION OF METHYL CHLORIDE WITH PHOSPHORUS TRICHLORIDE FOR THE PREPARATION OF METHYL PHOSPHONIC DICHLORIDE

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Clay-Kinnear-Perren complexes, prepared from the reaction of methyl chloride, phosphorus trichloride and aluminum chloride,^{1-3,14} are compounds from which several valuable organophosphorus intermediates containing P-C bonds (*e. g.* MeP(O)Cl₂, MeP(O)(OR)₂, MeP(S)Cl₂, and MePCl₂) are produced *via* hydrolysis,¹⁻⁶ alcoholysis,⁷ sulfurization,^{2,6} and reduction respectively.^{6,8-14}

The aluminum chloride-catalyzed alkylation of phosphorus trichloride with methyl chloride and the formation of a complex was first proposed by $Clay^1$ and Kinnear-Perren² and elaborated thereafter.³⁻⁵ It has been noted that the reaction can afford two types of complexes MePCl₄•AlCl₃ (1**a**) and MePCl₄•2AlCl₃ (1**b**)^{3,7}

MeCl + PCl₃ + nAlCl₃ \longrightarrow MePCl₄•nAlCl₃ $\xrightarrow{H_2O}$ MeP(O)Cl₂ 1 2 a) n = 1; b) n = 2

Treatment of solid product **1a** was considered to be very difficult in succeeding steps, whereas product **1b**, as a thick viscous liquid, was quite expensive due to the quantity of aluminium chloride required. The reactions were also known to be slow and time-consuming using methyl chloride under STP conditions.³ Attempts have been made for the preparation of **1a** as the sole product using a suspension of aluminum chloride in an excess of phosphorus trichloride (600 mol%). Under these conditions, in spite of a reaction temperature of 60-90°C and the use of pressurized methyl chloride in a pressure glass bottle, a reaction time of 14 h was required.¹⁴

The ionic nature of the complexes originally suggested by the discoverers of the method^{1,2} has been disputed by others.^{7,15} Identical ³¹P NMR spectra were reported⁷ for the two

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complexes but some authors have concluded that a very large up-field chemical shift of the phosphorus occurs in **1b** relative to **1a**.¹⁵

Hydrolysis of the complex afforded methyl phosphonic dichloride (2, MPDC), a key organophosphorus intermediate. Clay observed several important features which were crucial to experimental success of the hydrolysis reaction; these included (i) careful control of temperature at the onset of the reaction and (ii) addition of an exact amount of water, which should be a 7-11 molar ratio. Different methods of hydrolysis ($H_2O^{2,3}$ or 35% HCl (aq)¹) were applied to obtain the maximum yield. The hydrolysis agents were added dropwise at 0°C or below. The lower temperature (-20°C) was attained by addition of solid carbon dioxide to the solution. In another method, the solution of the complex was poured slowly on a mixture of crushed ice and solid carbon dioxide.⁵ It has been stated that the maximum overall yield of MPDC was obtained when hydrolysis of the dissolved complex was performed by adding all of the required water in 30 minutes or less. If the rate is slower than specified, the yield drops off sharply. In a pilot plant scale and at a low level of hydration, a hard, soft and sticky precipitate was formed in the solution and on the surfaces of cooling coils (interfering greatly with heat transfer), separation of which was very difficult. This precipitate was not formed when 10-11 moles of water per mole of aluminum chloride were added in 30 minutes or less. The solvent widely used for this process has been CH₂Cl₂, in which the complex is dissolved. Small-scale work showed that a much better hydrolysis was accomplished when the complex was in a true solution in CH₂Cl₂ rather than as a suspension and that 7 to 10 parts by weight of CH₂Cl₂ were necessary to ensure the dissolution. Although there is great interest in the utilization of this complex for the synthesis of further important organophosphorus intermediates, nevertheless the specific experimental details of the complex formation and hydrolysis steps remain unknown. Moreover, the parameters to optimize the consumption of aluminum chloride in the complex formation step and the factors preventing the formation of sticky precipitate and augmenting the yield in the hydrolysis step (except the amount of water and temperature) were not determined.

The manufacture of methyldichlorophosphine (MePCl₂) by the reaction of phosphorus trichloride with methane is a rational method by which methyl phosphonic dichloride (**MPDC**) is produced by an oxidation reaction. However, the reaction of phosphorus trichloride with methane is a vapor phase reaction carried out at high temperature (at least 500°C).¹⁶ Thus, the materials constituting the apparatus must be carefully selected and as the starting materials are chlorides, special precautions must be taken to prevent environmental pollution. In addition, not only is the reaction dangerous, but it produces many by-products making the separation of the desired product extremely difficult.

Therefore, we have reinvestigated the Friedel-Crafts reaction of pressurized methyl chloride with phosphorus trichloride and the hydrolysis of the complex formed in the preparation of methyl phosphonic dichloride (**MPDC**). The influence of parameters such as $AlCl_3/PCl_3$ molar ratio (1, 1.5 and 2), temperature, and time of reaction in the conversion rate of PCl₃ and

formation of MePCl₄•AlCl₃ (1a) and MePCl₄•2AlCl₃ (1b) were studied. In addition, the parameters such as the hydrolysis agent (H₂O or 35% aqueous HCl), AlCl₃/PCl₃ molar ratio, amount of organic solvent (CH₂Cl₂), and stirring were optimized in the hydrolysis step. The mixture of AlCl₃ and PCl₃ with molar ratio of 1.1 has formed a massive solid soaked with phosphorus trichloride. Injection of pressurized methyl chloride (P ~ 4.5 atm) in a pressure glass bottle containing the preceding mixture and starting the rotation of the stir bar on the surface of the mixture led to the formation of a viscous supernatant liquid (complex), the amount of which was increased and became the only phase present at the end of the reaction. The reaction of the mixture of phosphorus trichloride and aluminum chloride with methyl chloride was exothermic. Degassing methyl chloride dissolved in the reaction medium transformed the liquid complex to a glassy solid. The dissolution of the solid complex in CH₂Cl₂ was difficult and some precipitate was formed. In order to extract the complex from the reactor, it was dissolved in CH₂Cl₂ under pressure immediately after formation.

The conversion rate of phosphorus trichloride and formation of each constituent in the mixture were studied by ³¹P NMR spectroscopy using CH_2Cl_2 as solvent. Using different AlCl₃/PCl₃ molar ratios at 40°C for 2 h permitted recognition of two distinct signals at δ 118 and ~117.5 in CH₂Cl₂, the ratio of which was dependent on the AlCl₃/PCl₃ molar ratio (*Fig. 1*).



³¹P NMR spectra (in CH₂Cl₂) of the complexes formed from the reaction between AlCl₃, PCl₃ and MeCl with different AlCl₃/PCl₃ molar ratios at 40°C for 2 h a) AlCl₃/PCl₃ = 1; b) AlCl₃/PCl₃ = 1.5; c) AlCl₃/PCl₃ = 2

Fig. 1

With a AlCl₃/PCl₃ molar ratio of 1, a considerable amount of phosphorus trichloride (observed at δ 220) was left unchanged and a doublet appeared at δ 118 and ~117.5 with the predominance of the signal at δ 118 (*Fig. 1a*). With a AlCl₃/PCl₃ molar ratio of 1.5, a major part of phosphorus trichloride was reacted and an increase in intensity was observed for the signal at ~ δ 117.5 ppm (*Fig. 1b*). Complete disappearance of the signal due to phosphorus trichloride was observed when molar ratio of AlCl₃/PCl₃ was 2. In this case, a singlet appeared at ~ δ 117.5 ppm (*Fig. 1c*).

In this context, different conclusions have been made concerning chemical shifts of phosphorus in the two complexes. Some authors have estimated these to be very close⁷ and others to be very displaced.¹⁵ Our observations have permitted us to conclude that the presence of the signal at δ 118 ppm is due to **1a** and those at ~ δ 117.5 attributable to **1b**, which was produced after formation of **1a**. This was confirmed when we carried out the reaction with AlCl₃/PCl₃ molar ratio of 1.1 at several temperatures and different times (*Fig. 2*). At 50°C, the



³¹P NMR spectra (in CH₂Cl₂) of the complexes formed from the reaction between AlCl₃, PCl₃ and MeCl with a AlCl₃/PCl₃ molar ratio of 1.1 at different temperatures and reaction times
a) T = 50°C, t = 4.5 h; b) T = 25°C, t = 1 h; c) Continuation of the reaction in state b for 12 h at 40°C Fig. 2

conversion of phosphorus trichloride was not complete after 4.5 h, whereas two important signals appeared at δ 118 and ~117.5 (*Fig. 2a*). This led us to conclude that the simultaneous formation of **1a** and **1b** is responsible for the consumption of a major part of the aluminum chlo-

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ride and thus, a considerable amount of phosphorus trichloride (39%) remains unreacted. Interesting results were obtained when the reaction was performed at 25°C for 1 h. In this situation, in spite of time and temperature reduction, the conversion rate of phosphorus trichloride was increased (74%) with appearance of a singlet at δ 118 (*Fig. 2b*). Continuation of the reaction for 12 h at 40°C to attain maximum conversion of phosphorus trichloride was not successful, and some phosphorus trichloride (11%) remained in the mixture. A weak signal appeared at $\sim \delta$ 117.5 which is indicative of the formation of **1b** (*Fig. 2c*). These observations revealed that **1b** is formed above 25°C, and the reaction temperature should be controlled around 25°C to minimize its formation.

The hydrolysis of the complex was performed in CH₂Cl₂ as solvent, using water and 35% aqueous HCl as hydrolysis agents. The effects of the amount of solvent and hydrolysis agent in the yield of MPDC were studied using ³¹P NMR spectroscopy with POCl, as internal standard. The hydrolysis of the complex was very exothermic and the temperature of the reaction mixture was kept at 0°C by means of a water-ice bath. Addition of the hydrolysis agent was adjusted to 0.20-0.25 mL/min. Vigorous liberation of gaseous HCl - decreasing with the time was observed at the beginning of the hydrolysis where a milky suspension was formed in the solution. At the end of the procedure, the finely dispersed suspension of hydrated aluminum chloride coagulated suddenly to form the granules of 3-4 mm, readily separable from the rest of the mixture. The amount of hydrolysis agent necessary for the process is of great importance since, if more is used than necessary, it causes the hydrolysis of the product (MPDC) and also deforms the aluminum chloride hydrate to a sticky viscous precipitate, the separation of which is difficult. The optimized amount of hydrolysis agent was determined using a solution of the complex (0.025 M) in CH₂Cl₂ containing POCl₃ (0.025 M) as internal reference. The yield of MPDC was compared with POCI, present in solution using ³¹P NMR spectroscopy. The results are outlined in Fig. 3. In this manner, we have determined the optimum amount of hydrolysis agent necessary to carry out the hydrolysis.

Increasing the amount of CH_2Cl_2 also increased the yield of **MPDC** (*Table 1*). Therefore, the yield is dependent upon the amount of solvent.

rable 1. Complex II	1901.019515 1.1610	Using Different Amounts of C11, C1, as Solvent		
Ē	Entry	Solvent (mL)	Yield (%)	
	1	CH_2Cl_2 (15)	49	
	2	CH_2Cl_2 (25)	54	
	3	$CH_2Cl_2(35)$	59	
		and the second		

Table 1. Complex Hydrolysis^a Yield^b Using Different Amounts of CH₂Cl₂ as Solvent

a) Complex formation was carried out with 0.025 mol of PCl₃ and with a AlCl₃/PCl₃ molar ratio of 1.76. The hydrolysis reactions were performed with 8 mL of H₂O (0.20-0.25 mL/min). b) Based on ³¹P NMR spectroscopy.



Complex^a hydrolysis yield^b with different amounts of H₂O^c and 35% aqueous HCl^d a) Hydrolysis reactions were done in 0.025 M scale and hydrolysis agent addition rate was 0.20-0.25 mL/min; b) Based on ³¹P NMR spectroscopy; c) Molar ratio of AlCl₃/PCl₃ was 1.77; d) Molar ratio of AlCl₃/PCl₃ was 1.5. Fig. 3

After optimization of the above parameters, the role of the hydrolysis agents and AlCl₃ molar ratio in the yield of **MPDC** were determined (*Table 2*). The hydrolysis of complexes, formed with different molar ratios of AlCl₃/PCl₃ (2, 1.5 and, 1.1), and using H₂O or 35% aqueous HCl as hydrolysis agents, revealed that the AlCl₃/PCl₃ molar ratio of 1.1 afforded the best yield of **MPDC** (*Table 2, entries 3 and 6*). These results indicate that 35% aqueous HCl is preferred for the hydrolysis process when the AlCl₃/PCl₃ molar ratio is greater than 1.1 (*Table 2, entries 1, 2, 4, and 5*). With a AlCl₃/PCl₃ molar ratio of 1.1, the use of H₂O or 35% aqueous HCl as the hydrolyzing agent showed the same results (*Table 2, entries 3 and 6*).

Another fact that affects strongly the hydrolysis process is the stirring. Effectively, the high speed stirring of the mixture (by a mechanical stirrer) during the addition of the hydrolysis agent was indispensable, without which the hydrated aluminum chloride coagulated to form a sticky precipitate that alter the mixing, cooling, and separation procedures.

Entry	AlCl ₃ /PCl ₃ molar ratio	Conversion rate of PCl ₃ (%)	Hydrolysis agent ^c (mL)	Yield ^d (%)			
1	2	100	H ₂ O (9)	44			
2	1.5	93	H ₂ O (7)	53			
3	1.1	70	H ₂ O (4.8)	68			
4	2	100	35% HCl (11.8)	56			
5	1.5	92	35% HCl (9)	65			
6	1.1	67	35% HCl (6.3)	67			

Table 2. Complex Hydrolysis Yield^a with Different AlCl₃/PCl₃ Molar Ratios^b Using H₂O and 35% HCl(aq) as Hydrolysis Agents

a) Based on weighed **MPDC** and on the molar conversion rate of PCl_3 . b) Complex formations were carried out with 0.025 mol of PCl_3 . c) The hydrolysis agent addition rate was 0.20-0.25 mL/min. d) Based on ³¹P NMR spectroscopy.

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In conclusion, it was found that rapid reaction of pressurized gaseous methyl chloride occurred with the molar mixture of aluminum chloride and phosphorus trichloride, without any need for a sophisticated reactor. ³¹P NMR characterization of the two complexes have permitted us to determine the temperature dependency of complex formation (**1a** or **1b**) and established the optimized conditions under which, with a minimum amount of catalyst (aluminum chloride), a maximum conversion rate of phosphorus trichloride was obtained. Thus, the synthesis of MePCl₄•AlCl₃ (**1a**) was accomplished in 0.1 molar scale with AlCl₃/PCl₃ molar ratio of 1.1 under 4.5 atmospheres at 25°C for 2 h with 95% conversion of PCl₃. In the hydrolysis step and for a AlCl₃/PCl₃ molar ratio greater than 1.5, 35% aqueous HCl seemed to be the more appropriate hydrolysis agent. It has been found that for a AlCl₃/PCl₃ molar ratio of 1.1, water is as effective as 35% aqueous HCl in the hydrolysis process which afforded - after evaporation of solvent (CH₂Cl₂) - **MPDC** (61% yield) of ~98% purity.

EXPERIMENTAL SECTION

NMR spectra were recorded on a Bruker DPX-250 instrument (250 MHz for ¹H, 62.5 MHz for ¹³C and 100 MHz for ³¹P). CDCl₃ and CH₂Cl₂ were used as solvents; chemical shifts are reported in δ (ppm) from TMS (¹H and ¹³C) and 85% H₃PO₄ (³¹P), with downfield shifts positive. GC-MS spectrum was obtained on a Varian (GC; Star 3400 *CX*, MS; Saturn 4D) using DB-5MS column (0.1 micron; 30 m x 0.25 mm). Only m/z values having intensities of more than 20% are given, and retention time is reported with a column temperature of 200°C and an He flow rate of 10 mL/min.

Preparation of Complex MePCl₄•AlCl₃ (1a).- Into a 250 mL, pressure glass bottle was placed 18.7 g (0.137 mol) of AlCl₃ and 11 mL (0.125 mol) of PCl₃. A one-inch magnetic stir bar was placed upon the surface of the mixture (a massive solid soaked with phosphorus trichloride), and then pressurized methyl chloride (P = 4.5 atm at 25°C) was introduced in to the pressure glass bottle. Starting the rotation of the stir bar upon the surface of the mixture and controlling the temperature at 25°C caused the gradual formation of a supernatant viscous liquid. After 2 h, 96% of the initial phosphorus trichloride charge had been consumed.

Hydrolysis of the Complex 1a.- After the preparation of the complex with gaseous methyl chloride (preceding experiment), 225 mL of CH_2Cl_2 were added to the mixture to dissolve the complex. Instantly, some white precipitate formed. The suspension was transferred to a 500 mL, three-necked flask equipped with a condenser, an addition funnel and a mechanical stirrer, immersed in a water-ice bath at 0°C. The hydrolysis of this mixture was performed using 25 mL of water, added dropwise (1 mL/min), with vigorous stirring (1000 rpm) of the mixture until the milky suspension - first produced - suddenly coagulated to form granules (3-4 mm in diameter). The solution was then filtered, and the filtrate was evaporated *in vacuo* on a water-bath; the residue was allowed to crystallize to give 10.1 g (61%) of **MPDC** of 98% purity. ¹H NMR (CDCl₃): δ 2.53 (d, J = 15 Hz) (*lit.*¹⁷ δ 2.28 and 16.4 Hz). {¹H}¹³C NMR (CDCl₃): d 30.2 (d, J = 101 Hz) (*lit*.¹⁸ δ 97 and 104 Hz). ³¹P NMR (CDCl₃): δ 44.0 (q, J = 15 Hz) [*lit*. δ 43.5 in THF^{19a} (δ 44.5 in CCl₄ and 44.0 in CDCl₃¹⁷) and 16.4 Hz^{19b}]. MS: retention time = 2.7 min; m/z (intensity (%)): 47 (100), 97 (98), 99 (32), 117 (22), 132 (35), 133 (M⁺, 49), 134 (21), 135 (31).

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