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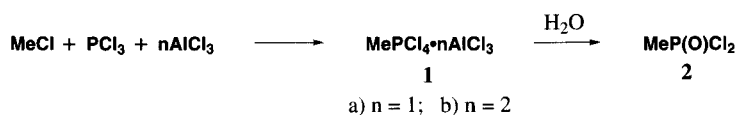
**REEXAMINATION OF THE FRIEDEL-CRAFTS REACTION OF  
METHYL CHLORIDE WITH PHOSPHORUS TRICHLORIDE  
FOR THE PREPARATION OF METHYL PHOSPHONIC DICHLORIDE**

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

The aluminum chloride-catalyzed alkylation of phosphorus trichloride with methyl chloride and the formation of a complex was first proposed by Clay<sup>1</sup> and Kinnear-Perren<sup>2</sup> and elaborated thereafter.<sup>3-5</sup> It has been noted that the reaction can afford two types of complexes MePCl<sub>4</sub>•AlCl<sub>3</sub> (**1a**) and MePCl<sub>4</sub>•2AlCl<sub>3</sub> (**1b**)<sup>3,7</sup>



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.<sup>3</sup> 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.<sup>14</sup>

The ionic nature of the complexes originally suggested by the discoverers of the method<sup>1,2</sup> has been disputed by others.<sup>7,15</sup> Identical <sup>31</sup>P NMR spectra were reported<sup>7</sup> for the two

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

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 ( $\text{H}_2\text{O}^{2,3}$  or 35%  $\text{HCl}$  (aq)<sup>1</sup>) were applied to obtain the maximum yield. The hydrolysis agents were added dropwise at  $0^\circ\text{C}$  or below. The lower temperature ( $-20^\circ\text{C}$ ) 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.<sup>5</sup> 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  $\text{CH}_2\text{Cl}_2$ , 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  $\text{CH}_2\text{Cl}_2$  rather than as a suspension and that 7 to 10 parts by weight of  $\text{CH}_2\text{Cl}_2$  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.

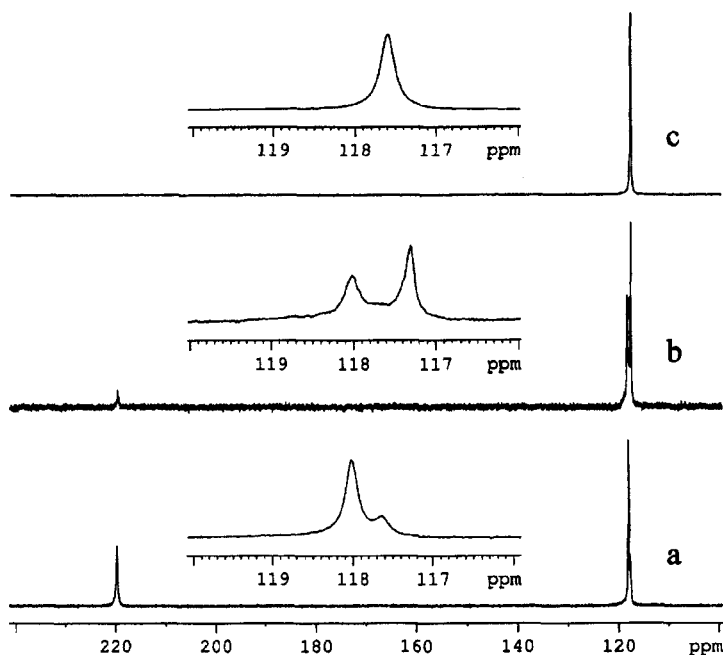
The manufacture of methyldichlorophosphine ( $\text{MePCl}_2$ ) by the reaction of phosphorus trichloride with methane is a rational method by which methyl phosphonic dichloride (**MPDC**) is produced by an oxidation reaction. However, the reaction of phosphorus trichloride with methane is a vapor phase reaction carried out at high temperature (at least  $500^\circ\text{C}$ ).<sup>16</sup> 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  $\text{AlCl}_3/\text{PCl}_3$  molar ratio (1, 1.5 and 2), temperature, and time of reaction in the conversion rate of  $\text{PCl}_3$  and

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formation of  $\text{MePCl}_4 \cdot \text{AlCl}_3$  (**1a**) and  $\text{MePCl}_4 \cdot 2\text{AlCl}_3$  (**1b**) were studied. In addition, the parameters such as the hydrolysis agent ( $\text{H}_2\text{O}$  or 35% aqueous  $\text{HCl}$ ),  $\text{AlCl}_3/\text{PCl}_3$  molar ratio, amount of organic solvent ( $\text{CH}_2\text{Cl}_2$ ), and stirring were optimized in the hydrolysis step. The mixture of  $\text{AlCl}_3$  and  $\text{PCl}_3$  with molar ratio of 1.1 has formed a massive solid soaked with phosphorus trichloride. Injection of pressurized methyl chloride ( $P \sim 4.5$  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  $\text{CH}_2\text{Cl}_2$  was difficult and some precipitate was formed. In order to extract the complex from the reactor, it was dissolved in  $\text{CH}_2\text{Cl}_2$  under pressure immediately after formation.

The conversion rate of phosphorus trichloride and formation of each constituent in the mixture were studied by  $^{31}\text{P}$  NMR spectroscopy using  $\text{CH}_2\text{Cl}_2$  as solvent. Using different  $\text{AlCl}_3/\text{PCl}_3$  molar ratios at  $40^\circ\text{C}$  for 2 h permitted recognition of two distinct signals at  $\delta$  118 and  $\sim 117.5$  in  $\text{CH}_2\text{Cl}_2$ , the ratio of which was dependent on the  $\text{AlCl}_3/\text{PCl}_3$  molar ratio (*Fig. 1*).

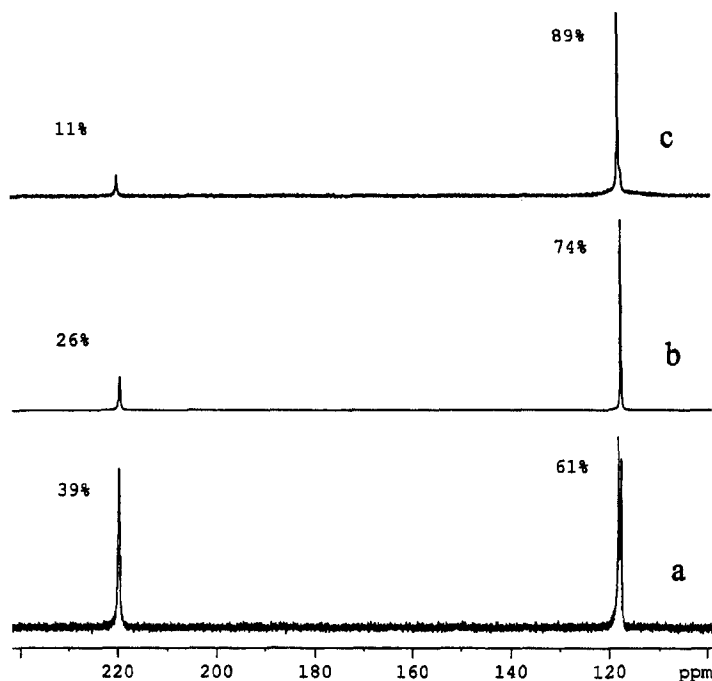


$^{31}\text{P}$  NMR spectra (in  $\text{CH}_2\text{Cl}_2$ ) of the complexes formed from the reaction between  $\text{AlCl}_3$ ,  $\text{PCl}_3$  and  $\text{MeCl}$  with different  $\text{AlCl}_3/\text{PCl}_3$  molar ratios at  $40^\circ\text{C}$  for 2 h  
 a)  $\text{AlCl}_3/\text{PCl}_3 = 1$ ; b)  $\text{AlCl}_3/\text{PCl}_3 = 1.5$ ; c)  $\text{AlCl}_3/\text{PCl}_3 = 2$

**Fig. 1**

With a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1, a considerable amount of phosphorus trichloride (observed at  $\delta$  220) was left unchanged and a doublet appeared at  $\delta$  118 and  $\sim$ 117.5 with the predominance of the signal at  $\delta$  118 (*Fig. 1a*). With a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.5, a major part of phosphorus trichloride was reacted and an increase in intensity was observed for the signal at  $\sim$  $\delta$  117.5 ppm (*Fig. 1b*). Complete disappearance of the signal due to phosphorus trichloride was observed when molar ratio of  $\text{AlCl}_3/\text{PCl}_3$  was 2. In this case, a singlet appeared at  $\sim$  $\delta$  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 close<sup>7</sup> and others to be very displaced.<sup>15</sup> Our observations have permitted us to conclude that the presence of the signal at  $\delta$  118 ppm is due to **1a** and those at  $\sim$  $\delta$  117.5 attributable to **1b**, which was produced after formation of **1a**. This was confirmed when we carried out the reaction with  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.1 at several temperatures and different times (*Fig. 2*). At 50°C, the



**<sup>31</sup>P NMR spectra (in  $\text{CH}_2\text{Cl}_2$ ) of the complexes formed from the reaction between  $\text{AlCl}_3$ ,  $\text{PCl}_3$  and  $\text{MeCl}$  with a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.1 at different temperatures and reaction times**  
 a)  $T = 50^\circ\text{C}$ ,  $t = 4.5$  h; b)  $T = 25^\circ\text{C}$ ,  $t = 1$  h; c) Continuation of the reaction in state b for 12 h at  $40^\circ\text{C}$

**Fig. 2**

conversion of phosphorus trichloride was not complete after 4.5 h, whereas two important signals appeared at  $\delta$  118 and  $\sim$ 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  $\delta$  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.

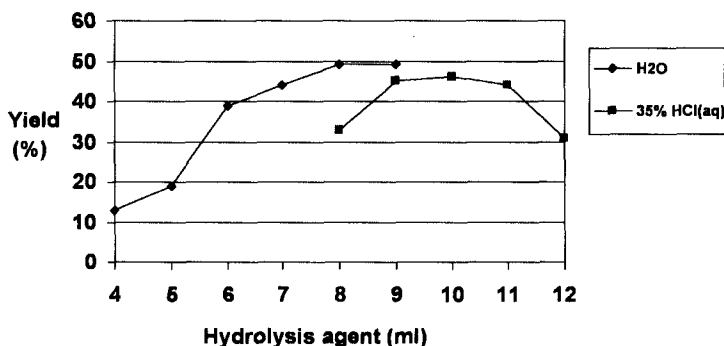
The hydrolysis of the complex was performed in  $\text{CH}_2\text{Cl}_2$  as solvent, using water and 35% aqueous HCl as hydrolysis agents. The effects of the amount of solvent and hydrolysis agent in the yield of MPDC were studied using  $^{31}\text{P}$  NMR spectroscopy with  $\text{POCl}_3$  as internal 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  $\text{CH}_2\text{Cl}_2$  containing  $\text{POCl}_3$  (0.025 M) as internal reference. The yield of MPDC was compared with  $\text{POCl}_3$  present in solution using  $^{31}\text{P}$  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  $\text{CH}_2\text{Cl}_2$  also increased the yield of MPDC (Table 1). Therefore, the yield is dependent upon the amount of solvent.

**Table 1. Complex Hydrolysis<sup>a</sup> Yield<sup>b</sup> Using Different Amounts of  $\text{CH}_2\text{Cl}_2$  as Solvent**

| Entry | Solvent (mL)                  | Yield (%) |
|-------|-------------------------------|-----------|
| 1     | $\text{CH}_2\text{Cl}_2$ (15) | 49        |
| 2     | $\text{CH}_2\text{Cl}_2$ (25) | 54        |
| 3     | $\text{CH}_2\text{Cl}_2$ (35) | 59        |

a) Complex formation was carried out with 0.025 mol of  $\text{PCl}_3$  and with a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.76. The hydrolysis reactions were performed with 8 mL of  $\text{H}_2\text{O}$  (0.20-0.25 mL/min). b) Based on  $^{31}\text{P}$  NMR spectroscopy.



Complex<sup>a</sup> hydrolysis yield<sup>b</sup> with different amounts of H<sub>2</sub>O<sup>c</sup> and 35% aqueous HCl<sup>d</sup>

- 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 <sup>31</sup>P NMR spectroscopy; c) Molar ratio of AlCl<sub>3</sub>/PCl<sub>3</sub> was 1.77; d) Molar ratio of AlCl<sub>3</sub>/PCl<sub>3</sub> was 1.5.

Fig. 3

After optimization of the above parameters, the role of the hydrolysis agents and AlCl<sub>3</sub> molar ratio in the yield of MPDC were determined (Table 2). The hydrolysis of complexes, formed with different molar ratios of AlCl<sub>3</sub>/PCl<sub>3</sub> (2, 1.5 and, 1.1), and using H<sub>2</sub>O or 35% aqueous HCl as hydrolysis agents, revealed that the AlCl<sub>3</sub>/PCl<sub>3</sub> 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 AlCl<sub>3</sub>/PCl<sub>3</sub> molar ratio is greater than 1.1 (Table 2, entries 1, 2, 4, and 5). With a AlCl<sub>3</sub>/PCl<sub>3</sub> molar ratio of 1.1, the use of H<sub>2</sub>O 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.

Table 2. Complex Hydrolysis Yield<sup>a</sup> with Different AlCl<sub>3</sub>/PCl<sub>3</sub> Molar Ratios<sup>b</sup> Using H<sub>2</sub>O and 35% HCl(aq) as Hydrolysis Agents

| Entry | AlCl <sub>3</sub> /PCl <sub>3</sub> molar ratio | Conversion rate of PCl <sub>3</sub> (%) | Hydrolysis agent <sup>c</sup> (mL) | Yield <sup>d</sup> (%) |
|-------|---|---|------------------------------------|------------------------|
| 1     | 2   | 100                                     | H <sub>2</sub> O (9)               | 44                     |
| 2     | 1.5   | 93                                      | H <sub>2</sub> O (7)               | 53                     |
| 3     | 1.1   | 70                                      | H <sub>2</sub> 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                     |

- a) Based on weighed MPDC and on the molar conversion rate of PCl<sub>3</sub>. b) Complex formations were carried out with 0.025 mol of PCl<sub>3</sub>. c) The hydrolysis agent addition rate was 0.20-0.25 mL/min. d) Based on <sup>31</sup>P 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.  $^{31}\text{P}$  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  $\text{MePCl}_4 \cdot \text{AlCl}_3$  (**1a**) was accomplished in 0.1 molar scale with  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.1 under 4.5 atmospheres at  $25^\circ\text{C}$  for 2 h with 95% conversion of  $\text{PCl}_3$ . In the hydrolysis step and for a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio greater than 1.5, 35% aqueous HCl seemed to be the more appropriate hydrolysis agent. It has been found that for a  $\text{AlCl}_3/\text{PCl}_3$  molar ratio of 1.1, water is as effective as 35% aqueous HCl in the hydrolysis process which afforded - after evaporation of solvent ( $\text{CH}_2\text{Cl}_2$ ) - **MPDC** (61% yield) of ~98% purity.

### EXPERIMENTAL SECTION

NMR spectra were recorded on a Bruker DPX-250 instrument (250 MHz for  $^1\text{H}$ , 62.5 MHz for  $^{13}\text{C}$  and 100 MHz for  $^{31}\text{P}$ ).  $\text{CDCl}_3$  and  $\text{CH}_2\text{Cl}_2$  were used as solvents; chemical shifts are reported in  $\delta$  (ppm) from TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), 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  $200^\circ\text{C}$  and an He flow rate of 10 mL/min.

**Preparation of Complex  $\text{MePCl}_4 \cdot \text{AlCl}_3$  (**1a**).**- Into a 250 mL, pressure glass bottle was placed 18.7 g (0.137 mol) of  $\text{AlCl}_3$  and 11 mL (0.125 mol) of  $\text{PCl}_3$ . 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  $25^\circ\text{C}$ ) 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  $25^\circ\text{C}$  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  $\text{CH}_2\text{Cl}_2$  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  $0^\circ\text{C}$ . 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.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.53 (d,  $J = 15$  Hz) (*lit.*<sup>17</sup>  $\delta$  2.28 and 16.4 Hz).  $\{^1\text{H}\}^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): d 30.2 (d,  $J =$



101 Hz) (*lit.*<sup>18</sup>  $\delta$  97 and 104 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  44.0 (q, J = 15 Hz) [*lit.*  $\delta$  43.5 in THF<sup>19a</sup> ( $\delta$  44.5 in CCl<sub>4</sub> and 44.0 in CDCl<sub>3</sub><sup>17</sup>) and 16.4 Hz<sup>19b</sup>]. MS: retention time = 2.7 min; m/z (intensity (%)): 47 (100), 97 (98), 99 (32), 117 (22), 132 (35), 133 (M<sup>+</sup>, 49), 134 (21), 135 (31).

## REFERENCES

1. J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951); *US Patent* 2,744,132; *Chem. Abstr.*, **51**, 1246c (1956).
2. A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952); *GB Patent* 707,961; *Chem. Abstr.*, **49**, 7588f (1954).
3. T. P. Hignett, L. B. Hein and A. B. Phillips, *US Patent* 2,875,245; *Chem. Abstr.*, **53**, 12177a (1959).
4. P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 3379 (1953).
5. T. L. Siddall and C. A. Prohaska, *J. Org. Chem.*, **28**(10), 2908 (1963).
6. G. Lindner, P. O. Granbom and K. Bergqvist, FOA (*Foersvarets Forskningsanst.*) Rep., **4** (1970); *Chem. Abstr.*, **73**, 131085m (1970).
7. F. W. Hoffmann, T. C. Simmons and L. J. Glunz, *J. Am. Chem. Soc.*, **79**, 3570 (1957).
8. M. Soroka, *Synthesis* 450 (1977).
9. Y. Ogawa, H. Yoshida, S. Inoue and T. Niida, *Meiji Seika Kenkyu Nempo*, **13**, 49 (1973); *Chem. Abstr.*, **81**, 37788m (1974).
10. R. Schliebs and H. Kaiser, *Ger. Offen. DE Patent* 1,119,860; *Chem. Abstr.*, **58**, 6863d (1963).
11. L. Schmerling, *US Patent* 2,986,579; *Chem. Abstr.*, **55**, 20961a (1961).
12. V. G. Gruzdev, S. Z. Ivin and K. V. Karavanov, *Zh. Obshch. Khim.*, **35**, 1027 (1965).
13. B. J. Perry, J. B. Reesor and J. L. Ferron, *Can. J. Chem.*, **41**, 2299 (1963).
14. H. Tsuchiya, S. Nabekawa and M. Takada, *US Patent* 4,857,238; *Chem. Abstr.*, **112**, 21147z (1990).
15. C. Symmes and L. D. Quin, *J. Org. Chem.*, **43**(6), 1250 (1978).
16. K. Gehrman, A. Ohorodnik, J. Rosenthal and S. Schafer, *Ger. Offen. DE Patent* 3,149,937; *Chem. Abstr.*, **99**, 176058h (1983).

## PREPARATION OF METHYL PHOSPHONIC DICHLORIDE

17. L. Maier *Helv. Chim. Acta*, **56**, 492 (1973).
18. G. Mavel and M. J. Green, *Chem. Commun.*, 742 (1968).
19. (a) K. Moedritzer, L. Maier and L. C. D. Groenweghe, *J. Chem. Eng. Data*, **7**, 307 (1962).  
(b) J. F. Nixon and R. Schmutzler, *Spectrochimica Acta*, **22**, 565 (1966).

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