# SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL DIALKYLPHOSPHINOUS CHLORIDES<sup>1</sup>

## J. L. FERRON

### ABSTRACT

A series of compounds with the generalized formula RR'PCl have been obtained by the metal (antimony or zinc) reduction of [RR'PCl<sub>2</sub>]+[AlCl<sub>4</sub>]<sup>-</sup>. The yields of symmetrical and unsymmetrical dialkylphosphinous chlorides obtained by this method are superior to those obtained in previous syntheses.

### INTRODUCTION

The original synthesis of symmetrical dialkylphosphinous chlorides ( $R = C_2H_{51}$ , *i*- $C_3H_{71}$ )  $i-C_4H_9$ ) has been the pyrolysis of  $R_3PCl_2$  (1),

 $R_{3}PCl_{2} \xrightarrow{\text{heat}} R_{2}PCl + RCl.$ 

The diethyl analogue has also been obtained in 38% yield by the action of lead tetraethyl upon ethylphosphonous dichloride (2),

 $C_2H_5PCl_2 + (C_2H_5)_4Pb \rightarrow (C_2H_5)_2PCl + (C_2H_5)_3PbCl.$ 

The complex resulting from alkyl chlorides, phosphorus trichloride, and aluminum chloride was first prepared by Clay (3) and formulated as

 $RC1 + PCl_3 + AlCl_3 \rightarrow [RPCl_3]^+ [AlCl_4]^-$ 

The above complexes have been used in these laboratories for the preparation of alkylphosphonous dichlorides (4). These dichlorides have been obtained in good yield when the aluminum chloride complex is dissolved in a high-boiling electron-donating solvent such as diethyl phthalate (DEP) and reduced with antimony powder. The diethyl phthalate apparently forms a more stable complex with the aluminum chloride and the liberated RPCl<sub>4</sub> is then reduced by the antimony powder as follows:

> $[RPCl_3]^+[AlCl_4]^- + DEP \rightarrow [DEP][AlCl_3] + RPCl_4$  $3RPCl_4 + 2Sb \rightarrow 3RPCl_2 + 2SbCl_3$ .

Since then Ivin and Karavanov (5) have shown that alkylphosphonous dichlorides react with aluminum chloride in an analogous fashion,

 $RPCl_2 + AlCl_3 + R'Cl \rightarrow [RR'PCl_2][AlCl_4],$ 

and it occurred to us that the reduction of this complex might provide a simple and direct route to dialkylphosphinous chlorides. The reduction of a DEP solution of these aluminum chloride complexes by zinc dust at room temperature or by antimony powder at 75-80° C has provided dialkylphosphinous chlorides in yields of 60-73%.

## EXPERIMENTAL

### Apparatus

The apparatus used is shown in the figure and allows dialkylphosphinous chlorides to be prepared and distilled without coming in contact with air. The 10/30 Standard

<sup>1</sup>Manuscript received December 19, 1960. Contribution from the Chemistry Section, Suffield Experimental Station, Ralston, Alberta. Work carried out under Defence Research Board Project No. D52-20-20. This paper constitutes Suffield Technical Paper No. 206.

Can. J. Chem. Vol. 39 (1961)

#### FERRON: SYNTHESIS DIALKYLPHOSPHINOUS CHLORIDES



FIG. 1. Apparatus for the preparation of dialkylphosphinous chlorides.

Taper joint carries a thermometer and the 19/38 joint can be used for fitting an inlet tube, a dropping funnel, a bleed for distillations under reduced pressure, or for adding the powdered metal for the reduction. The 28/15 ball joint, J, accommodates the dry ice condenser (upper right of figure) during methyl chloride addition, or a watercooled condenser during the addition of less volatile alkyl chlorides, as well as the distillation unit shown in the figure. Complexes described under (a) and (b) were formed in a pressure bottle and transferred into the flask R under a stream of dry N<sub>2</sub>; those described under (c) and (d) were formed at atmospheric pressure directly in the reaction vessel R. All reactions were carried out under a dry N<sub>2</sub> atmosphere.

### Reagents

Can. J. Chem. Downloaded from www.nrcresearchpress.com by USP – Universidade de Sao Paulo on 11/10/14 For personal use only.

All the reagents were of Reagent Grade and were used as supplied from the manufacturers without further purification. Antimony in lump form was ground in a mortar, pulverized in a ball mill, and sieved through a 250 mesh sieve immediately prior to use.

## (a) Preparation of Chloromethyl-methylphosphinous Chloride (ClCH<sub>2</sub>)(CH<sub>3</sub>)PCl

Aluminum chloride (100 g, 0.75 mole) was weighed directly into a pressure bottle and cooled in a dry ice-acetone mixture. To the cold contents were then added chloromethylphosphonous dichloride (113.8 g, 0.75 mole) and liquid methyl chloride (40 ml,

### CANADIAN JOURNAL OF CHEMISTRY, VOL. 39, 1961

0.80 mole). The bottle was stoppered and left standing at room temperature for 16 hours by which time the mixture had turned solid except for a small liquid layer in the bottom of the container. The contents were then heated at 100-102° C for a further 72 hours. After cooling in dry ice – acetone mixture the bottle was opened, the solid broken into pieces and transferred into the reaction flask R under a stream of dry N<sub>2</sub>. Diethyl phthalate (DEP) (500 ml) was then added and violent stirring maintained until the solid had completely dissolved. The solution was then degassed under reduced pressure (water vacuum) while the temperature was gradually raised to 60° C. After the solution was cooled to room temperature, dry  $N_2$  was admitted into the system, a dry ice-acetone cooling mixture placed under the receiver C, the wide-bore isolation stopcock closed, and the system evacuated to 0.1-0.5 mm. Finely powdered antimony (60.9 g, 0.5 mole) was added all at once through a Standard Taper joint, a bleed inserted, and the suspension vigorously stirred. The reaction flask R was rapidly evacuated by opening the wide-bore stopcock. The reduction of the complex by antimony was exothermic and the temperature rose slowly from 33° C to 49° C while the chloromethylmethylphosphinous chloride distilled over into the distillation flask C. When the evolution of heat had stopped, the temperature of the solution was brought up to 80-85° C with the help of a heating mantle and maintained in that range for  $\frac{1}{2}$  hour. After all the dialkylphosphinous chloride had been collected, dry  $N_2$  was admitted into the system, a bleed inserted in place of the stopper S, the isolation stopcock closed, and the product redistilled under reduced pressure, and the main fraction collected in one of the receivers. The yield of  $(ClCH_2)(CH_3)PCl$  (b.p. 59° C/9 mm) was 72 g (73%). Most of the dialkylphosphinous chlorides are very reactive and cannot be handled readily in an open atmosphere. Analyses are thus cumbersome to perform and most of the compounds prepared have been identified by the formation of derivatives.  $(ClCH_2)(CH_3)PCl$  was reacted with sulphur and the chloromethyl-methylthionophosphonic chloride analyzed. Calculated for (ClCH<sub>2</sub>)(CH<sub>3</sub>)P(S)Cl: C, 14.73%; H, 3.10%. Found: C, 14.84%; H, 3.20%.

# (b) Preparation of Dimethylphosphinous Chloride (CH<sub>3</sub>)<sub>2</sub>PCl

This compound was prepared on a 0.75 mole scale by mixing in the cold methylphosphonous dichloride, aluminum chloride, and methyl chloride in a pressure bottle and shaking the mixture at room temperature. The complex formed readily and after transfer of the solid into the flask R and solution in DEP, the reduction by antimony (60.9 g, 0.50 mole) at 85–90° C gave 43.7 g (60%) of dimethylphosphinous chloride (b.p. 72–74° C/697 mm). The oxygen addition compound was analyzed for identification purposes. Calculated for (CH<sub>3</sub>)<sub>2</sub>P(O)Cl: C, 21.35%; H, 5.38%. Found: C, 21.33%; H, 5.33%.

## (c) Preparation of Isopropyl-methylphosphinous Chloride (i-C<sub>3</sub>H<sub>7</sub>)(CH<sub>3</sub>)PCl

For this preparation the reaction flask R was fitted with a dropping funnel in the 19/38 Standard Taper joint and the dry-ice condenser on the 28/15 ball joint J. Aluminum chloride (66.7 g, 0.5 mole) was placed in the reaction flask and isopropylphosphonous dichloride (73.0 g, 0.5 mole) was added dropwise while stirring violently. The addition was exothermic and the aluminum chloride dissolved completely. The solution was cooled to room temperature and the dropping funnel replaced by an inlet tube extending below the surface of the liquid. Slow addition of gaseous methyl chloride was started while the temperature of the reaction mixture was kept below  $45^{\circ}$  C by intermittent immersion of the flask in a cold-water bath. The addition of methyl chloride was stopped after the reaction was completed as evidenced by a fast reflux rate of methyl chloride on the dry ice condenser. The addition was complete in approximately  $1\frac{1}{2}$  hours.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by USP – Universidade de Sao Paulo on 11/10/14 For personal use only.

cooling to room temperature, the complex was dissolved in DEP (300 ml), degassed under reduced pressure, and the reduction carried out in the usual way using a theoretical amount of freshly powdered antimony (40.5 g, 0.33 mole). The yield of isopropylmethylphosphinous chloride (b.p.  $82-85^{\circ} \text{ C}/208 \text{ mm}$ ) was 44.0 g (65.5%).

## (d) Preparation of Diisopropylphosphinous Chloride $(i-C_3H_7)_2PCl$

Aluminum chloride (68.5 g, 0.51 mole) was placed in the flask R and isopropylphosphonous dichloride (74.8 g, 0.52 mole) added dropwise, the temperature being kept below 30° C by occasional immersion in a dry ice-acetone cooling bath. After the aluminum chloride had dissolved, isopropyl chloride (40.5 g, 0.51 mole) was added dropwise maintaining the temperature below 30° C. After about two-thirds of the isopropyl chloride had been added, the reaction mixture became very viscous and stirring became inefficient. The addition of isopropyl chloride was stopped, methylene chloride (50 ml) was added after which the addition of isopropyl chloride was resumed. This addition could be carried out rapidly as no appreciable heat was evolved. Once the addition was completed, the solution was heated to reflux for 1 hour, cooled to room temperature, DEP (300 ml) added with stirring, and the solution degassed in the usual way. After degassing, zinc dust (32 g, 0.51 mole) was added and the suspension heated to 45° C. An exothermic reaction set in, the heating source was removed and the reaction mixture reached a temperature of 78° C. The liquid collected in flask C was then redistilled, giving a yield of 51.2 g (67.2%) of product (b.p. 69° C/697 mm).

## ACKNOWLEDGMENTS

The author is indebted to Mr. S. A. Gibbens for his technical assistance on the project, and to Mr. T. Stewart for the microanalytical work.

Thanks are due to the Chairman, Defence Research Board for kind permission to publish these results.

### REFERENCES

1. G. M. KOSOLAPOFF. Organophosphorus compounds. John Wiley & Sons, Inc., New York. 1950. pp. 42-51.
M. H. BEEBY and F. G. MANN. J. Chem. Soc. 172, 411 (1951).
J. P. CLAY. J. Org. Chem. 17, 892 (1952).
J. L. FERRON, B. J. PERRY, and J. B. REESOR. Nature, 188, 227 (1960).
S. Z. IVIN and K. V. KARAVANOV. J. Gen. Chem. U.S.S.R. 28, 2988 (1958). 2.

3.

4.

5.

## CORRECTIONS

Volume 39, 1961

Page 844. In line 22, "9 nun" should read "59 mm". Line 35, which reports analytical data, should be deleted.

Page 845. In line 20, "697 mm" should read "35 mm".

845