

A NEW METHOD FOR THE PREPARATION OF ALKANE PHOSPHONYL DICHLORIDES

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The alkane phosphonyl dichlorides (alkane dichlorophosphine oxides) are important as intermediates in the preparation of a variety of organo-phosphorus compounds. Methods for the preparation of these compounds were first reported independently by Hoffman (1) and Michaelis (2) in 1873. Since then several different methods have been reported by others (3-6). Most of these methods either are difficult, require reagents difficult of preparation, produce complicating side reactions, or are applicable only to special cases.

A new, simple method, applicable to the alkylation of phosphorus with primary, secondary, or tertiary alkyl groups, rendering a good yield of a product of high purity is described below. The method may be represented essentially by the following reactions:

1. $\text{RCl} + \text{PCl}_3 + \text{AlCl}_3 \rightarrow \text{RCl} \cdot \text{PCl}_3 \cdot \text{AlCl}_3$ (insoluble complex)
2. $\text{RCl} \cdot \text{PCl}_3 \cdot \text{AlCl}_3 + 7 \text{H}_2\text{O} \rightarrow \text{AlCl}_3 \cdot 6\text{H}_2\text{O} + \text{RPOCl}_2 + 2 \text{HCl}$

Several factors are important. These factors are: (a) order of mixing reagents; (b) control of temperature; (c) anhydrous condition of the reagents and apparatus; (d) molal ratio of water to complex used in the hydrolysis.

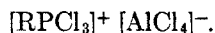
It was found that reaction 1 did not take place readily if the AlCl_3 was dissolved in the alkyl chloride before the PCl_3 was added. This difficulty was eliminated by mixing the PCl_3 with the AlCl_3 , then adding the alkyl chloride.

The temperature of reaction 1 must be controlled at near the reaction temperature to prevent side reactions. This is especially true in the preparation of secondary and tertiary alkyl products. It is highly important to control the temperature of reaction 2 in the case of the hydrolysis of primary alkyl complexes, lest the dichloride be further hydrolyzed to the corresponding acid. Secondary and tertiary alkane phosphonyl dichlorides are less readily hydrolyzed.

The molal ratio of H_2O to complex being hydrolyzed must be within the limits of 7:1 to 11:1, or very poor yields will result.

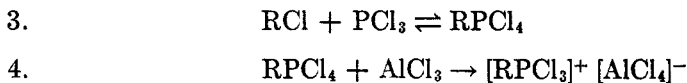
The method of removing AlCl_3 from another complex, as in reaction 2, has been previously reported by Dye (7).

The nature of the complex formed has not been fully investigated; further study is under way. However, its high heat stability (melting point of the $\text{C}_2\text{H}_5\text{Cl} \cdot \text{PCl}_3 \cdot \text{AlCl}_3$ is approximately 370°) and the fact that solutions of the complex in nitromethane conduct an electric current and produce an abnormal lowering of the freezing point are indicative of its ionic nature and suggest a formula such as



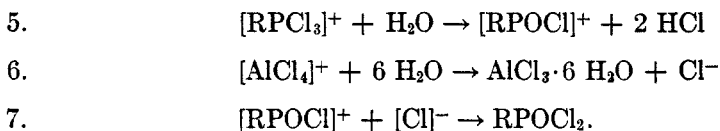
The compound AlPCl_3 is described (8) as having an ionic structure.

Since the complex does not form readily when the alkyl halide is allowed to dissolve the AlCl_3 before the addition of the PCl_3 , the mechanism of the complex formation may proceed in the following manner:



Reaction 3 has been reported (9).

A possible mechanism to account for the simultaneous hydrolysis and hydration of the complex may be expressed by the following reactions:



EXPERIMENTAL

Reagents. All reagents used, with the exceptions noted, were of reagent grade from the Fischer Scientific Company, New York. Isopropyl chloride and *tert*-butyl chloride were prepared from the alcohols by well-known methods. All of the alkyl chlorides used were redistilled over anhydrous calcium chloride. The apparatus used was dried at 105° and cooled in a desiccator just prior to use.

(a) *Preparation of ethyl phosphonyl dichloride.* First, 13.3 g. of anhydrous AlCl_3 was weighed into a glass-stoppered bottle, followed by 13.7 g. of PCl_3 . To this mixture was added 19.3 g. of ethyl chloride, and the bottle was closed and placed in a shaking machine. (All reagents and the reaction bottle were cooled in a refrigerator at approximately 4° just prior to weighing and mixing. Up to the moment of closing the bottle the temperature of the mixture had risen to 9° .)

After 15 minutes' shaking, the temperature of the mixture had risen to 23° . At this temperature the solid AlCl_3 dissolved, accompanied by a sudden rise in temperature which reached approximately 35° . The solution became pale yellow in color. After about 12 minutes the temperature dropped to 25° , accompanied by the deposit of a white crystalline precipitate. The shaking of the mixture was continued for one hour. The reaction bottle was then placed in a refrigerator at approximately 4° . After 24 hours the supernatant liquid was poured off, leaving 18 g. of dry crystalline material, m.p. 370° (approximately). A solution of the complex in nitromethane was found to exhibit an electrical conductivity equivalent to that of a univalent salt in water.

Hydrolysis of the complex $\text{C}_2\text{H}_5\text{Cl} \cdot \text{PCl}_3 \cdot \text{AlCl}_3$. This crystalline complex was dissolved in 200 ml. of methylene chloride, transferred to a three-necked 500-ml. flask, cooled to 0° , and hydrolyzed by adding dropwise (at the rate of 10 drops per minute) 25.3 ml. of cold concentrated hydrochloric acid (4°). The mixture was stirred for two hours, beginning with the addition of the first drop of hydrochloric acid. The reaction flask was immersed in an ice-water mixture which kept the temperature between 0° to 7° throughout the hydrolysis. The cold mixture was filtered and the filtrate was distilled to remove excess solvent, followed by vacuum-distillation of the residue at 28 mm. The vacuum-distillate yielded 7.6 g. of a colorless liquid, b.p. 174.5° .

Anal. Calculated: Cl, 48.3; Organic P, 21.0.

Found: Cl, 47.9; Organic P, 20.8.

The substance reacted with water at 25° with approximately the vigor shown by PCl_3 ; however, it reacted very slowly in an ice-water mixture. These characteristics serve to identify the material as $\text{C}_2\text{H}_5\text{POCl}_2$. The lead salt of the acid, $\text{C}_2\text{H}_5\text{PO}(\text{OH})_2$, was prepared by warming the aqueous solution of the hydrolytic product of $\text{C}_2\text{H}_5\text{POCl}_2$ with $\text{Pb}(\text{OH})_2$, after removal of the chloride with AgNO_3 .

(b) *Preparation of isopropyl phosphonyl dichloride.* To 26.1 g. of AlCl_3 in a three-necked flask, equipped with a thermometer, stirrer, and reflux condenser was added 26.8 g. of PCl_3 . The flask was cooled to 10° and 44.6 g. of isopropyl chloride was added. The mixture was stirred while the temperature was allowed to rise gradually until the reaction started at about 15° . The temperature was maintained at less than 25° . Even at 25° some brownish degradation products appeared, accompanied by the evolution of HCl . The reaction was complete in 15 minutes. At this time the flask was half-filled with a white crystalline complex discolored at some points where the temperature had risen too high. The material was stored overnight in a refrigerator at 4° , then subjected to reduced pressure (30 mm.) at 25° to remove excess isopropyl chloride. The residue was dissolved in 170 ml. of CH_2Cl_2 , cooled to -5° , and hydrolyzed by the dropwise addition of 44 ml. of cold conc'd HCl over 85 minutes, the mixture being stirred vigorously all the while. After a quick filtration, 12.2 g. (38.6%) of isopropyl phosphonyl dichloride was recovered from the filtrate upon vacuum distillation. This distillate was a colorless liquid, b.p. 76° at 23 mm., which was immiscible with water and hydrolyzed very slowly at room temperature, but more rapidly with hot water (50°).

Anal. Calculated: Cl, 44.1; Organic P, 19.2.

Found: Cl, 43.9; Organic P, 19.1.

(c) *Preparation of tert-butyl phosphonyl dichloride.* The method used was exactly as described in (b). Quantities used were 33.3 g. of AlCl_3 , 34.35 g. of PCl_3 , and 46.2 g. of *tert*-butyl chloride. The reaction began at 11° and was complete in 10 minutes; yield of the complex, 99%. The complex was hydrolyzed with 57 ml. of conc'd HCl at temperatures between -10° and 5° in 150 ml. of methylene chloride. A yield of 19.3 g. (44%) of *tert*-butyl phosphonyl dichloride, was recovered by vacuum-distillation. The material is a white, wax-like solid, m.p. 123° , subliming at 110° at 25 mm. It has a distinct camphor-like odor, does not hydrolyze even with hot water but does react readily with water when dissolved first in ethyl alcohol.

Anal. Calculated: Cl, 40.5; Organic P, 17.7; M.W., 175.04.

Found: Cl, 40.4; Organic P, 17.5; M.W. (in benzene), 176.1.

CONCLUSIONS

A new method for the preparation of alkane phosphonyl dichlorides has been described which is applicable to alkylation with primary, secondary, and tertiary alkyl groups.

The mechanism of the reactions involved in this method has been postulated.

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