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The Preparation of 2-Chloroalkane-1-phosphonic Acid

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It is well known that 2-chloroalkane-1-phosphonic acid is a phosphorylation reagent[1,2] and a useful intermediate for the preparation of 1-alkane-1-phosphonic acid.[3]

The preparation of 2-chloroalkane-1-phosphonic acid or 1-alkene-1-phosphonic acid by the reaction of phosphorus pentachloride with a terminal olefin such as styrene derivatives has been reported by many investigators,[4] but in most cases the yields were unsatisfactory because of the side reaction. The yields of the desired products by this procedure usually ranged between 40—50%.

In the present experiments, it has been found that 2-chloroalkane-1-phosphonic acid can be prepared in a high yield by adding an adequate amount of phosphorus trichloride to the reaction medium. (see Table 1)

Table 1. The results of the reaction of octene-1 and phosphorus pentachloride[a]

Exp. No.	PCl_3/PCl_5	Time (hr)	Conversion[b] (%)	Yield (%) I	Yield (%) II
1	0	24	97	49	41
2	0.2	24	58	47	7
3	1	24	56	50	1
4	1	24	42	39	0
5	9	24	30	27	0
6	1	72	99	92	2
7	2	72	97	93	0

a) The PCl_5/octene-1 ratio was 2:1; benzene was used as the solvent, and the total volume of benzene+PCl_3 was maintained at 300 m*l*. The reaction temperature was 25°C.

b) The yields of 2-chlorooctane-1-phosphonic acid (I) and 1,2-dichlorooctane (II) were based upon the amount of octene-1 employed. The conversions of octene-1 were calculated from the amounts of them recovered.

When a larger amount of phosphorus trichloride was added to the reaction mixture, the rate of the reaction became much slower and the formation of 1,2-dichlorooctane was much suppressed. When the reaction time was lengthened to 72 hr, the conversion of the olefin increased to 97% and 2-chlorooctane-1-phosphonic acid was obtained in a 93% yield.

The reaction mechanism of the formation of 2-chloroalkane-1-phosphonic acid is considered to proceed *via* Eqs. (1) and (2):[5]

$$2PCl_5 \rightleftarrows PCl_4^+ + PCl_6^- \quad (1)$$

$$PCl_4^+ + CH_2{=}CHR \rightleftarrows PCl_4CH_2\overset{+}{C}HR \xrightarrow{Cl^-} PCl_4CH_2CHClR \quad (2)$$

1,2-Dichloroalkane may be produced by the addition of chlorine to the olefin by reactions (3) and (4).

$$PCl_5 \rightleftarrows PCl_3 + Cl_2 \quad (3)$$

$$Cl_2 + CH_2{=}CHR \longrightarrow ClCH_2CHClR \quad (4)$$

The equilibrium (3) may migrate to the left upon the addition of phosphorus trichloride, and the generation of chlorine may be suppressed; this latter may consequently decrease the formation of 1,2-dichlorooctane. When a large amount of phosphorus trichloride is present, the formation of the chloride is completely restrained and the side reaction (4) can be prevented. The slower rate of the reaction (2) may be due to the small concentration of PCl_4^+, caused by the nucleophilic attack of PCl_3 on PCl_4^+, as is shown in the reaction (5):

$$PCl_4^+ + PCl_3 \longrightarrow [PCl_4 \cdot PCl_3]^+ \quad (5)$$

Experimental

Preparation of 2-Chlorooctane-1-phosphonic Acid. Typical Procedure. Twenty-two grams (0.2 mol) of octene-1, 83.3 g (0.4 mol) of phosphorus pentachloride, 54.8 g (0.4 mol) of phosphorus trichloride, and 265 m*l* of absolute benzene were added to a 500 m*l*, three-necked flask fitted with a condenser protected by a drying tube. After the mixture had then been stirred for 24 hr, it was poured into ice water and stirred for 2 more hours. The oily layer was se-

1) J. A. Maynard and J. M. Swan, *Aust. J. Chem.*, **16**, 596 (1963).

2) V. M. Clark, *Proc. Chem. Soc.*, **1964**, 129.

3) Y. Okamoto, T. Nitta and H. Sakurai, *J. Oil Chemists' Soc. Japan*, **12**, 882 (1969).

4) G. M. Kosolapoff, "Organic Reactions," Vol. VI, ed. by R. Adams, John Wiley & Son, New York (1957), p. 273.

5) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing Co., New York (1967), p. 262.

parated, and the aqueous layer was extracted with ether. The oily layer and the ether extract were combined and distilled. After the ether had been removed by atmospheric pressure, the remainder was distilled under reduced pressure below 100°C. The distillate was a mixture of octene-1 (9.0 g, bp 87—89°C/250 mmHg) and 1,2-dichlorooctane (0.4 g, bp 80—81°C/1 mmHg, Found: Cl, 38.14; C, 52.52; H, 8.89%. Calcd for $C_8H_{16}Cl_2$: Cl, 38.72; C, 52.46; H, 8.81%). From the residue, 22.8 g of pure 2-chlorooctane-1-phosphonic acid (mp 85—86°C. Found: P, 12.89; Cl, 14.81; C, 40.11; H, 7.53%. Calcd for $C_8H_{18}ClP$: P, 12.92; Cl, 14.79; C, 40.09; H, 7.57%) were obtained by recrystallization from petroleum ether.