# Pyridyl Phosphates From the Reaction of Sodium Pyridinates, Dialkyl Phosphite and Carbon Tetrachloride

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A convenient method for preparing pesticidal pyridyl phosphates from the reaction of sodium halopyridinates, dialkyl phosphite and carbon tetrachloride is described. The dialkyl phosphonato anion as an intermediate in this reaction is proposed.

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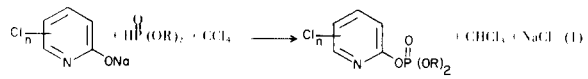
Halopyridyl phosphates or thiophosphates are well known pesticides. They are conventionally prepared by reacting a phosphorochloridate or phosphorochloridothioate with the sodium or ammonium pyridinate (1).

Recently, it was observed in this laboratory that the halopyridyl phosphates can be obtained in an excellent yield by the reaction of sodium halopyridinates, dialkyl phosphite and carbon tetrachloride. The reaction is expressed as follows:



That the above reaction is not a free radical process (2) is shown by the fact that the addition of cuprous chloride, ferrous chloride or 9,10-dihydroanthracene neither enhanced nor hindered the halopyridyl phosphate formation. In addition, no reaction between dimethyl phosphite and carbon tetrachloride was observed with or without photochemical irradiation.

Carrying out the reaction between dimethyl phosphite and carbon tetrachloride with a base catalyst, such as triethylamine, in an nmr tube proved that the products are the phosphorochloridate and chloroform. Steinberg reported (3) the synthesis of diethyl, dipropyl, and dibutyl phosphorochloridates from the corresponding dialkyl phosphites based on the same reaction. The reaction is depicted as follows:

$$HP(OCH_3)_2 + CCl_4 \xrightarrow{Et_3N} ClP(OCH_3)_2 + CHCl_3 \quad (2)$$

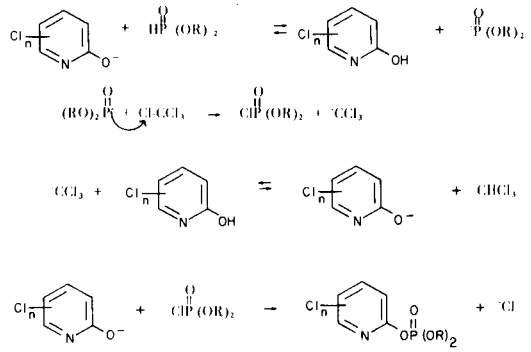
The use of chloroform instead of carbon tetrachloride in the above reaction did not give the phosphorochloridate, probably due to the fact that $^-CCl_3$ is a good leaving group while $^-CHCl_2$ is not. This observation helps to explain the attack of $^-P(OCH_3)_2$ on the chlorine of carbon tetrachloride rather than on carbon, and leads us to propose the following mechanism for the reaction (2):

$$HP(OCH_3)_2 + Et_3N \rightleftharpoons {}^-P(OCH_3)_2 + Et_3\overset{+}{N}H$$

$$(CH_3O)_2P + Cl\text{-}CCl_3 \rightarrow ClP(OCH_3)_2 + {}^-CCl_3$$

$$Et_3\overset{+}{N}H + {}^-CCl_3 \rightleftharpoons Et_3N + CHCl_3$$

In the reaction (1), the pyridyloxy anion itself acts as the base catalyst. It is also observed by nmr that the addition of pyridinate to dimethyl phosphite reduces the proton peak (adjacent to P) in dimethyl phosphite without affecting the other two methyl protons. Based on the above observations, the following mechanism for reaction (1) is proposed:



## EXPERIMENTAL

Diethyl 3,5-Dichloro-2-pyridyl phosphate.

Sodium 3,5-dichloro-2-pyridinate (16.4 g., 0.1 mole) and 100 g., of carbon tetrachloride were placed into a 250 ml. three-necked flask equipped with a stirrer, reflux condenser and thermometer. The mixture was heated to 40° and 13.6 g. (0.1 mole) of diethyl phosphite was added in a single portion. The temperature of the

reaction mixture was kept below 50° by the application of outside water cooling (the exotherm subsides in 0.5 hour). The heat of reaction was measured to be -37 Kcal/mole. Two hours after the addition of diethyl phosphite, the reaction mixture was washed with 100 ml. of water to remove the sodium chloride byproduct. The two layers were separated and the organic layer was distilled under a reduced pressure of 50 mm Hg to complete dryness. The crude product which weighed 28.5 g. (95%) was recrystallized once from 2-propanol to give 24.8 g. (82.7%) of white crystalline product, m.p. 37-38° (lit. (1,4,5) 37-38°).

Dimethyl 3,5-Dichloro-2-pyridyl Phosphate.

Dimethyl 3,5-dichloro-2-pyridyl phosphate was prepared from sodium 3,5-dichloro-2-pyridinate, carbon tetrachloride and dimethyl phosphite in the same manner as described in the preparation of diethyl 3,5-dichloro-2-pyridylphosphate. A white crystalline solid, m.p. 48-49° (lit. (5) 48-49°) was obtained in 85% yield.

Dimethyl 3,5,6-Trichloro-2-pyridyl Phosphate.

Dimethyl 3,5,6-trichloro-2-pyridyl phosphate was prepared from sodium 3,5,6-trichloro-2-pyridinate, carbon tetrachloride and dimethyl phosphite in the same manner as described in the preparation of diethyl 3,5-dichloro-2-pyridyl phosphate. A white prismatic crystal having a melting point of 90-92°, (lit. (5,6) 89-92°) was obtained in 82% yield.

Diethyl 3,5,6-Trichloro-2-pyridyl Phosphate.

Diethyl 3,5,6-trichloro-2-pyridyl phosphate was prepared from sodium 3,5,6-trichloro-2-pyridinate, carbon tetrachloride and diethyl phosphite in the same manner as described in the preparation of diethyl 3,5-dichloro-2-pyridyl phosphate. A white crystalline solid, m.p. 42-44° (lit. (5) 42-44°), was obtained in 89% yield.

Diethyl 2-Pyridyl Phosphate.

Diethyl 2-pyridyl phosphate was prepared from sodium 2-pyridinate, carbon tetrachloride and diethyl phosphite in the same manner as described in the preparation of diethyl 3,5-dichloro-2-pyridyl phosphate. After the removal of a low boiling substance, a light clear oil, $N_D^{15}$ 1.4612 (lit. (5) 1.4612), was obtained in 81% yield.

Base Catalyzed Reaction Between Carbon Tetrachloride and Dimethyl Phosphite.

In an nmr tube was placed a 10% solution of dimethyl phosphite in carbon tetrachloride. The nmr spectrum of the mixture indicated a proton peak at $\delta$ = 0.9 (H adjacent to P) and two $CH_3$ proton peaks at $\delta$ = 3.6 and 3.8. The spectrum did not change over two hours with or without photochemical irradiation. A couple of drops of triethylamine was added to the mixture in the nmr tube. Five minutes later, a spectrum was taken which showed a significant reduction in the peak size of protons at $\delta$ = 0.9, 3.6 and 3.8, with an appearance of three new peaks, $\delta$ = 3.7 and 3.9 corresponding to the methyl protons of dimethyl phosphorochloridate and $\delta$ = 7.5 corresponding to the proton of chloroform. The peaks at $\delta$ = 0.9, 3.6 and 3.8 decreased with time, while the peaks at $\delta$ = 3.7, 3.9 and 7.5 increased. One hour after the addition of triethylamine, all of the proton peaks at $\delta$ = 0.9, 3.6 and 3.8 had disappeared.

## REFERENCES AND NOTES

(1) R. H. Rigterink, U. S. Patent 3,244,586 (1966).

(2) W. J. Lautenberger, E. N. Jones and J. G. Miller, *J. Am. Chem. Soc.*, **90**, 1110 (1968).

(3) G. M. Steinberg, *J. Org. Chem.*, **15**, 637 (1950).

(4) R. H. Rigterink and E. E. Kenaga, *J. Agr. Food Chem.*, **14**, 394 (1966).

(5) T. Nishimura, I. Okuda and M. Yoshido, U. S. Patent 3,686,191 (1972).

(6) C. S. Wang and M. J. Mintz, U. S. Patent 3,928,370 (1975).