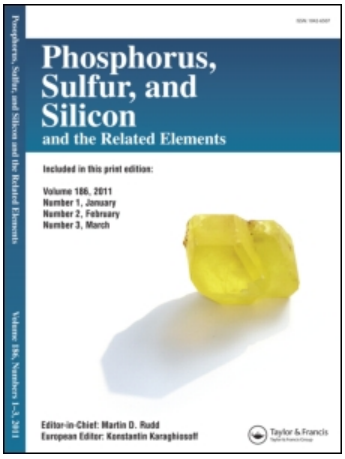

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SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF 4-METHYLPHENYL ESTERS OF DIMETHYL PHOSPHORAMIDOCHLORIDIC ACID AND DIMETHYL PHOSPHORAMIDOFLUORIDIC ACID

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SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF 4-METHYLPHENYL ESTERS OF DIMETHYL PHOSPHORAMIDOCHLORIDIC ACID AND DIMETHYL PHOSPHORAMIDOFLUORIDIC ACID

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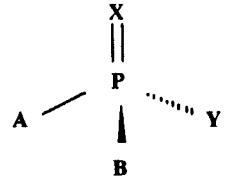
Synthesis of 4-methylphenyl esters of N,N-dimethyl phosphoramidochloridic acid (**1**) and N,N-dimethyl phosphoramidofluoridic acid (**2**) is reported. 18-Crown-6 with potassium fluoride was found an effective reagent for the conversion of **1** to **2**. These compounds were characterized by using ^{1}H, ^{31}P NMR, infrared and mass spectroscopic data. Analysis of the ^{1}H NMR spectrum of ester **1** gives a long-range ^{31}P-^{1}H spin spin coupling ($^{7}J_{P-H}$ = 1.2 Hz). A possible explanation for this unusual seven-bond coupling is discussed. In this study, a reasonable correlation between ^{31}P chemical shifts and P=O vibration frequencies is suggested.

Key words: Phosphoramidofluoridic acid, NMR, mass spectra, insecticides.

INTRODUCTION

Following the pioneering work by Schrader in 1940, several thousand organophosphorus compounds are known to act as insecticide and about 200 of these are or have been manufactured commercially.[1] In addition, they find numerous applications as plasticizers, flame retardants, reagents in the preparation of organophosphorus polymers, in solvent extraction of heavy metals.[1,2] As proposed by Schrader,[3] these insecticides have the general formula:



where X = O or S, A and B = alkyl, alkoxy, amino and Y = F, CN, SH, etc. Some of the compounds are extremely toxic to humans while others are relatively harmless and almost non-toxic. In general, the toxicity of an organophosphorus compound depends on its molecular structure so that comparatively small differences in chemical constitution, sometimes determine whether a compound is toxic

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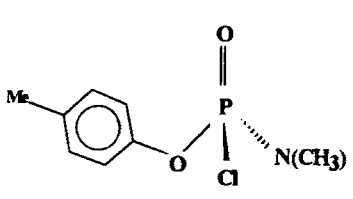
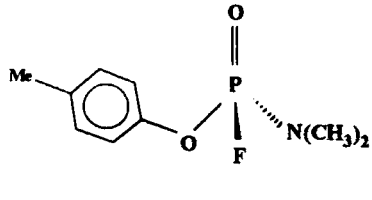
or non-toxic. Furthermore, these compounds show a wide range of properties.[1-4] For example, di-isopropyl fluorophosphate (DFP) has neurotoxic action, however as an opthalmic ointment (Dyflos) is used in the treatment of glaucoma.[5] Dimefox can be used in soil as an acaricide[1,3] while tricresyl phosphate (TCP) is non-toxic and is widely used as a plasticizer and petroleum additive.[1,2]

This preparation in high yield of organosphosphorus compounds containing different A, B, X and Y groups (in above formula) presents a number of problems of interest from a synthetic, kinetic and mechanistic standpoint. The major impetus for this activity is due to the intrinsic importance of nucleophilic substitutions at the phosphorus central atom and investigation of the structural correlations with bond characteristics in these compounds.[1-4]

We wish to report the synthesis and characterization of the previously unreported 4-methylphenyl esters of dimethyl phosphoramidochloridic acid (**1**) and dimethyl phosphoramidofluoridic acid (**2**) in fairly high yield.



(1)



(2)

EXPERIMENTAL

Caution! Although no poisoning observed during these studies, organophosphorus compounds have potentially neurotoxic action. They should be handled only with proper safety precautions.

General Information: Chemicals were obtained from Fluka or Merck and used without further purification. Sodium salt of *p*-cresol was prepared as described in the literature.[6] N,N-dimethyl phosphoramido dichloride was prepared by the method described elsewhere.[7] ^1H, ^{19}F, ^{31}P NMR spectra were recorded on a Bruker AC-80 FT-NMR spectrometer and reported in ppm. ^1H and ^{31}P chemical shifts are recorded relative to TMS and 85% H_3PO_4 (external), respectively. All NMR spectra were obtained at 23°C. Elemental analysis was performed using a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded on Bruker IFS-88 FT-IR spectrometer. Mass spectra were obtained from a Finnegan 8430 mass spectrometer.

Synthesis

N,N-dimethyl phosphoramidochloridic acid, 4-methyl phenyl ester (**1**): To a well-stirred solution of N,N-dimethyl phosphoramido dichloride (120 mmol) in *n*-hexan (200 ml) maintained at 15°C, was added sodium salt of *p*-cresol (100 mmol). Following this addition, the mixture was stirred for 1 h. After filtration, the solvent evaporated and an oily residue was obtained. By adding ether (40 ml) and standing overnight, colorless crystals of **1** were obtained. It was purified by recrystallization in ether-petroleum ether (1:1), yield 18.9 g (85%), mp 31-32°. Anal. Calc. for $C_9H_{13}ClNO_2P$: C, 46.2; H, 5.6; N, 5.9. Found: C, 46.7; H, 5.8; N, 6.1.

N,N-dimethyl phosphoramidofluoridic acid, 4-methyl phenyl ester (**2**): N,N-dimethyl phosphoramidochloridic acid (10 mmol) and KF (30 mmol) in the presence of 18-Crown-6 (1.5 mmol) was refluxed for 5 h in benzene (50 ml). The reaction mixture was worked up in the following manner: the mixture was cooled down to room temperature, and filtered. After evaporation of the solvent under vacuum, residue allowed to run through a long but narrow silica gel column eluted with $CHCl_3$. The first fraction eluted was collected and after evaporation of solvent a yellow oil was obtained. Anal. Calc. for $C_9H_{13}FNO_2P$: C, 49.7; H, 6.0; N, 6.4. Found: C, 49.8; H, 6.2; N, 6.5

Spectroscopic Data

$(CH_3)_2NP(O)(Cl)C_6H_5CH_3$ (**1**). Mass spectrum (70 ev) m/e, (fragment) [relative intensity]: 233 (M^+) [54], 198 ($M\text{-}Cl^+$) [18], 126 ($M\text{-}C_7H_7^+$) [38], 108 ($C_7H_7O^+$) [100], 44 ($C_2H_6N^+$) [88]. Infrared spectrum (NaCl, cm^{-1}): 3041 (w), 3014 (w), 2860 (w), 1606 (w), 1506 (s), 1271 (s), 1198 (m), 1105 (w), 999 (s), 951 (m), 822 (m), 582 (m). NMR spectra: ^{31}P ($CDCl_3$) δ −11.95 (sept.); ^1H ($CDCl_3$) δ 2.23 (d, J = 1.2 Hz), 2.81 (d, J = 13.7 Hz), 7.14.

$(CH_3)_2NP(O)(F)OC_6H_5CH_3$ (**2**). Mass spectrum (70 ev) m/e (fragment) [relative intensity]: 217 (M^+) [4], 85 ($H_3FO_2P^+$) [88], 84 ($H_2FO_2P^+$) [36], 83 (HFO_2P^+) [100], 82 (FO_2P^+) [4], 50 (FP^+) [4]. Infrared spectrum (NaCl, cm^{-1}); 3506 (w), 2929 (m), 2864 (m), 1608 (w), 1508 (s), 1288 (s), 1203 (s), 1122 (w), 1011 (s), 951 (s), 870 (s), 825 (s), 737 (m). NMR spectra: ^{31}P ($CDCl_3$) δ +6.1 (d, J = 967.64 Hz, obtained from ^{19}F spectrum); ^1H ($CDCl_3$), δ 2.30, 2.78 (d, J = 10.58 Hz of d, J = 1.92 Hz), 7.10.

RESULTS AND DISCUSSION

Method of Synthesis

Methods for the preparation of organophosphorus compounds containing P—F bonds are commonly divided into two pages. The first group employed $POCl_3$ and certain of its derivatives followed by subsequent fluorination using classic regents such as NaF. Second standard procedure uses phosphorus oxyfluorides (POF_3, $POClF_2$ and $POCl_2F$) as starting materials. Olah and Oswald[9] already reported the preparation of a series of aryl esters of phosphoramidofluoridothioic acid from $POCl_2F$ as starting material. It is obvious that reagents used in the second type can not offer the advantages such as ready accessibility and simplicity in operation. Apart from this, some aryl esters of dimethyl phosphoramidochloridic acid hitherto unreported in the literature, therefore the more attractive route can be stated to involve the reaction sequence.

$$POCl_3 + (CH_3)_2NH\cdot HCl \rightarrow (CH_3)_2NPOCl_2 + 2HCl$$

$$(CH_3)_2NPOCl_2 + ArONa \rightarrow (CH_3)_2NP(O)(OAr)Cl + NaCl$$

$$(CH_3)_2NP(O)(OAr)Cl \rightarrow (CH_3)_2NP(O)(OAr)F$$

However incorporation of fluorine into organophosphorus molecules by selective nucleophilic substitution of chlorine with the fluoride anion remains a difficult task (step 3). To find a suitable fluorinating agent, we investigated several common reagents. The results are summarized in Table I. As shown in Table I, KF/18-Crown-6 is a suitable agent for the preparation of **2** from **1** in fairly high yield. Although the use of KF/18-Crown-6 as fluorinating agent has been known for over 20 years, the specific use of this reagent for P—Cl to P—F conversion is novel. The reaction conditions are relatively mild and the conversion is essentially quantitative. It is likely that the same procedure can be used to prepare other aryl esters of N,N-dimethyl phosphoramidofluoridic acid.

Spectral Data

Spin-spin couplings (homo or hetero nuclear) higher than three bonds are less commonly observed and are interpreted by various models. Appreciable coupling constants ^7J(HH) and ^7J(FF) have been observed in fully conjugated systems, e.g., styrene[10] and fluorostyrenes.[11] Shaw and coworkers,[12] recently reported a seven-

TABLE I

The substitution of **1** with fluoride ion*

Reagent	Reflux time (h)	Yield % (GC)
NaF	5	46
KF	5	64
NaF/ 18-Crown-6	5	51
KF/ 18-Crown-6	5	92
KF- CaF_2**	5	26

* The molar ratio of substrate to KF was 1:3.

** Supported reagent was prepared according to ref [8].

TABLE II

J_{PNCH} values for the prepared compounds

Compound	$J_{P\text{-}N\text{-}C\text{-}H}$ (Hz)
$(CH_3)_2NP(O)Cl_2$	15.7
$(CH_3)_2NP(O)(Cl)OC_6H_5CH_3$	13.7
$(CH_3)_2NP(O)(F)OC_6H_5CH_3$	10.59

TABLE III

P=O stretching frequencies and ^{31}P chemical shifts for prepared compounds

Compound	$\delta(^{31}P)$ ppm	$\nu(P=O)$ cm^{-1}
$(CH_3)_2NP(O)Cl_2$	-19.1	1267
$(CH_3)_2NP(O)(Cl)OC_6H_5CH_3$	-11.95	1271
$(CH_3)_2NP(O)(F)OC_6H_5CH_3$	+6.1	1288

bond coupling $^7J(PP)$ in the azine diphosphine. Long-range ^{31}P-^1H spin-spin couplings in benzyl and tolyl phosphorus compounds were reported previously[13] and an overlap hyperconjugation coupling mechanism was considered for this behavior.

However, existence of $^7J_{P—H}$ (= 1.2 Hz) in compound **1** and its absence in **2** can not be completely interpreted by such a mechanism. Furthermore this value is relatively larger than that for tricresyl phosphoate ($^7J_{P—H}$ = 0.9 Hz).[13] It is postulated that this characteristic depends on the bonding nature of the phosphorus atom. The substitution of fluorine for chlorine in ester **1** causes the $d_\pi - p_\pi$ contribution in P—N and P—O bonds to decrease. This leads to a relative decrease in the multiple bonding between P—N and P—O—Ar in contrast to the increased multiple bonding from fluorine to phosphorus ($J_{P—F}$ = 967.64 Hz). The general trend in the magnitude of J_{PNCH} of the prepared compounds (cf. Table II) and similar compounds[14–17] is in agreement with this suggestion.

This qualitative argument can also be extended to ^{31}P chemical shifts in these compounds. As shown in Table III, these data support the changes in substituents to phosphorus bonding. On the other hand, in the series, $Me_2NP(O)Cl_2$ ($\nu_{P=O}$ = 1267 cm^{-1}), $Me_2NP(O)(F)OC_6H_5CH_3$ ($\nu_{P=O}$ = 1271 cm^{-1}), and $Me_2NP(O)(F)OC_6H_5CH_3$ ($\nu_{P=O}$ = 1288 cm^{-1}), there is an obvious increase in P=O vibration frequencies. This is in agreement with results previously reported by Wagner who found that PO bond characters are directly related to electronegativities of the Y group in symmetrically substituted phosphoryl compounds, POY_3.[18]

Therefore it is not surprising that an increase of the PO vibration frequency follows the upfield shift in ^{31}P resonance of these compounds (Table III).

However, the proof will be investigated in more detail.

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