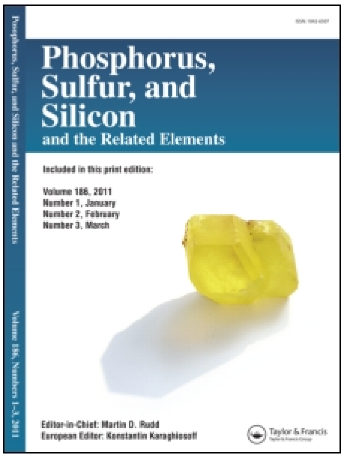

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SYNTHESIS OF PHOSPHONIC DICHLORIDES AND CORRELATION OF THEIR P-31 CHEMICAL SHIFTS

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SYNTHESIS OF PHOSPHONIC DICHLORIDES AND CORRELATION OF THEIR P-31 CHEMICAL SHIFTS

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Various mono-substituted diethyl arylphosphonates were prepared in good yield by treatment of aryl bromides or iodides with triethyl phosphite in the presence of $NiCl_2$ or alternatively, addition of the aryl grignard reagent to diethyl phosphorochloridate. These esters were then converted into the appropriate phosphonic dichlorides by standard methods. *Para*-substituted phosphonic dichlorides were also prepared by dimethylsulfoxide oxidation of phosphonous dichlorides which were prepared by Friedel–Crafts reaction of PCl_3 with the substituted benzene. The P-31 chemical shifts of these phosphonic dichlorides were correlated with Hammett (σ^n) and Taft (σ^0) values. The shielding of the phosphorus resonance signal by electron withdrawing groups was rationalized by increased P=O bonding. The observed shielding of *ortho*-substituted arylphosphonic dichlorides was rationalized by a gamma effect.

INTRODUCTION

Recently, we needed a variety of mono-substituted aryl-phosphonic dichlorides in our laboratory. We would now like to report the large scale syntheses of these derivatives[1] and correlation of their P-31 chemical shifts with empirical parameters.

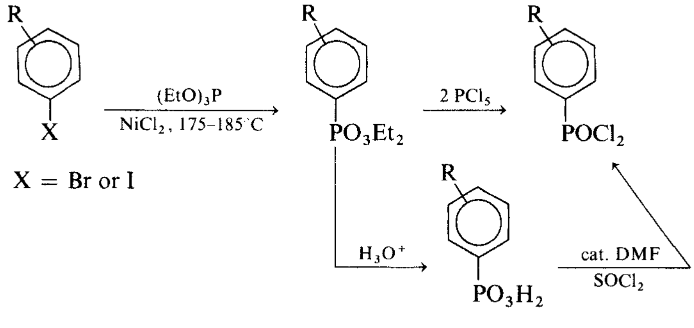
RESULTS AND DISCUSSION

A general route to these phosphonic dichlorides from the corresponding aryl bromides or iodides is outlined in Scheme I.

Treatment of these aryl halides with triethyl phosphite in the presence of anhydrous $NiCl_2$ according to the procedure described by Tavs[2] produced the appropriate diethyl arylphosphonates[3] in good yields as shown in Table I. These results expand the scope of the Tavs reaction[2] and illustrate its wide applicability to phosphorus chemistry.

Treatment of these diesters with two equivalents of PCl_5 yielded the phosphonic dichlorides in excellent yields (see Table IV). An alternative approach involved hydrolysis to yield the phosphonic acids[3] (see Table II), which were then converted into the acid chlorides with $SOCl_2$ containing catalytic amounts of N,N-dimethylformamide (DMF). In our hands, treatment of phosphonic acids with thionyl chloride containing no DMF yielded only phosphonic anhydrides.

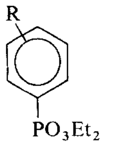
In several cases, the boiling point of the aryl bromide precluded the use of the Tavs reaction. However, addition of the Grignard reagent to an excess of diethyl phosphorochloridate[4] yielded the



SCHEME I

TABLE I

Preparation of diethyl arylphosphonates



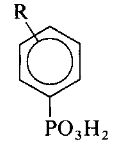
R[3]	Method[a]	Yield (%)	Bp[b] (°C)
p-CH_3	I	79	140
p-Cl	I	81	140
p-C_6H_5O	I	66	180
p-C_6H_5	I	80	150
p-CH_3S	I	88	150
m-CH_3	I	94	110
m-CH_3O	I	87	120
o-CH_3	I	89	120
o-CH_3O	I	82	120
p-CF_3	II	31	120
m-CF_3	II	93	120
m-F	II	60	100

[a] Method I represents the Tavs reaction[2], while method II is the reaction of the aryl Grignard reagent with diethyl phosphorochloridate.

[b] These values correspond to the temperature of the heating source during the bulb to bulb distillation under high vacuum (0.1–0.4 mm).

TABLE II

Preparation of arylphosphonic acids by hydrolysis

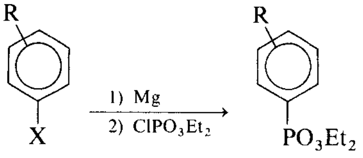


R	Yield (%)	Mp[b] (°C)	Reported[3] Mp (°C)
p-CH_3	98	185–7	187–9
p-Cl	89	184–6	187–8
p-F	88[a]	120–2	125–7
p-C_6H_5O	64	170–3	185[c]
p-CF_3	75	177–8	177–9
p-C_6H_5	90	235–40	218–20
p-CH_3S	82	186–9	242
m-CF_3	79	100–3	—
m-CH_3	88	119–20	121
m-CH_3O	96[a]	139–42	—
m-F	85[a]	95–8	—
o-CH_3O	26	179–82	179

[a] Hydrolysis of phosphonic dichloride.

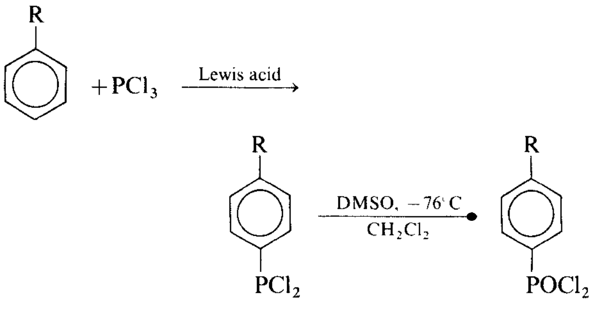
[b] Melting points are uncorrected.

[c] This is the mp of its hydrate.



SCHEME II

desired diethyl phosphonate[3] as illustrated in Scheme II. Formation of the Grignard reagent derived from *para*-bromobenzotrifluoride was accompanied by extensive tar formation. This result was puzzling, since the *meta*-substituted Grignard reagent was prepared without incident as demonstrated here and elsewhere.[5]

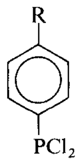


SCHEME III

Another method for preparing *para*-substituted arylphosphonic dichlorides is shown in Scheme III and involved the Friedel–Crafts reaction of PCl_3 with substituted benzene derivatives[6–9] (see Table III). The ortho isomers were not detected in the distilled phosphonous dichlorides as deduced by P-31 NMR spectroscopy. Oxidation of these phosphonous dichlorides with dimethylsulfoxide (DMSO) according to the procedure of Amonoo-Neizer and co-workers[10] produced the corres-

TABLE III

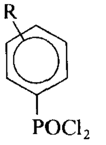
Preparation of *para*-substituted arylphosphonous dichlorides



R	Yield (%)	P-31 chemical shift (δ)
CH_3O[8]	61	—
F[6]	70	158.8 (J_{FP} = 4.8 Hz)
Me_2N[9]	20	164.5

TABLE IV

Preparation and physical properties of arylphosphonic dichlorides



R	Method of preparation[a]	P-31 chemical shift (δ)	Pertinent proton NMR data
H[b]	—	36.0	—
p-CH_3	I	36.5	CH_3, 2.45
p-Cl	I	34.0	—
p-C_6H_5O	I	35.2	—
p-C_6H_5	I	35.7	—
p-CH_3S	I	35.8	CH_3S, 2.5
p-CF_3	II	32.65	—
p-CH_3O	III	36.1	CH_3O, 3.98
p-F	III	33.9	—
p-$(CH_3)_2N$	III	37.6	$(CH_3)_2N$, 3.05
m-CH_3O	I	35.9	CH_3O, 3.9
m-CH_3	II	36.7	CH_3, 2.4
m-CF_3	II	30.7	—
m-F	II	32.9(J_{FP} = 9.8 Hz)	—
o-CH_3O	I	30.8	CH_3O, 4.0
o-CH_3	I	35.6	CH_3O, 2.75

[a] The roman numericals correspond to the method shown in the appropriate scheme.

[b] Commercially available from Aldrich Chemical Co.

ponding phosphonic dichlorides in good yields as shown in Table IV.

The purity of the phosphonic dichlorides was corroborated by phosphorus and proton NMR spectroscopy. The P-31 chemical shifts of these derivatives exhibited some consistent trends as shown in Table IV. The order of shielding of the *para* and *meta* substituted derivatives was the following

para $CF_3 > F > Cl > C_6H_5O > C_6H_5 >$
$CH_3S > CH_3O > H > CH_3 > Me_2N$

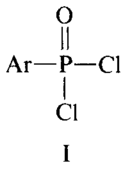
meta $CF_3 > F > CH_3O > H > CH_3$

The order of shielding in the *meta*-substituted arylphosphonic dichlorides was qualitatively dependent upon the electronegativity of the substituent. A least square fit of these P-31 chemical shifts with inductive parameters (σ_I)[11] exhibited a sample correlation coefficient of 0.82.

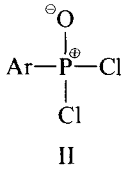
Correlation of P-31 chemical shifts with Hammett values has been demonstrated in one case.[12] Grim and Yankowsky[12] have shown that the P-31 chemical shifts of *para*-substituted triarylphosphines exhibited a slight correlation when the trimethylsilyl group was excluded. On the other hand, a Hammett plot (σ^n)[10] of the P-31 chemical shifts of these phosphonic dichlorides (Graph I) produced a reasonable fit (r = 0.90). Also, treatment of these data with Taft's σ^0 values[13] (Graph II) produced a slightly better correlation (r = 0.91).

These linear relationships are remarkable considering that σ values do not account for direct resonance interactions with phosphorus. On the contrary, the resonance interaction of the aryl ring with the dichlorophosphinyl group was negligible in most cases. The small discrepancies shown in Graphs I and II might be a reflection of these orbital perturbations.

The physical significance of these linear relationships might be interpreted in terms of resonance structures I and II. According to these data, structure I is the major resonance contributing


$\mathrm{Ar{-}P({=}O)(Cl){-}Cl}$

I


$\mathrm{Ar{-}P^{\oplus}(O^{\ominus})(Cl){-}Cl}$

II

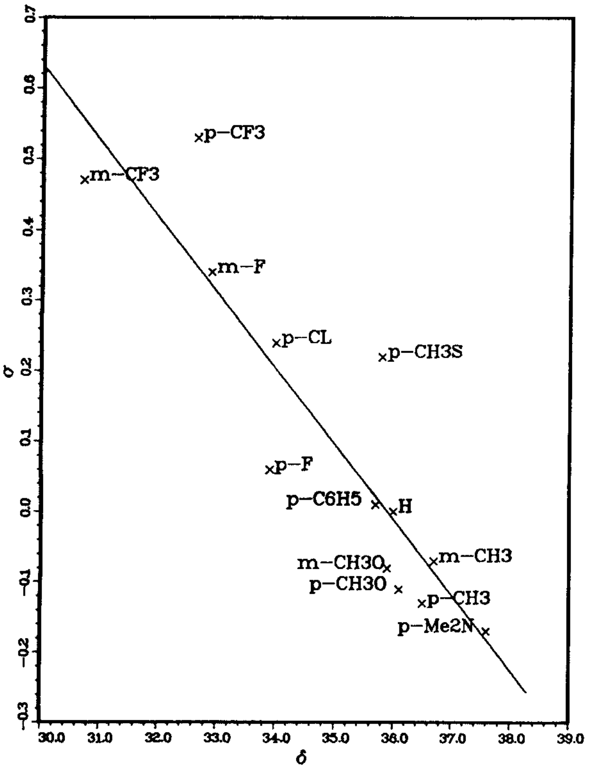


FIGURE 1 Plot of P-31 chemical shifts of substituted arylphosphonic dichlorides versus Hammett substituent constants.

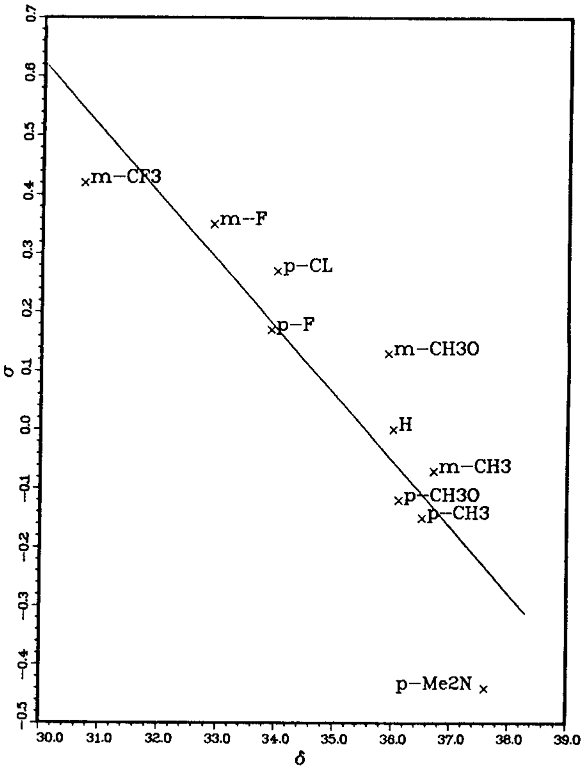
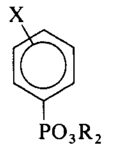


FIGURE 2 Plot of P-31 chemical shifts of substituted arylphosphonic dichlorides versus Taft substituent constants.

TABLE V

Elemental analyses of phosphonic acids and their diethyl esters



X	R	Calcd. C	Calcd. H	Found C	Found H
p-C_6H_5O	C_2H_5	62.74	6.25	62.78	6.31
p-C_6H_5	C_2H_5	66.20	6.60	66.32	6.68
m-CH_3O	C_2H_5	54.10	7.02	53.70	7.11
m-CF_3	C_2H_5	46.82	5.00	46.84	4.99
m-F	C_2H_5	51.73	6.08	51.57	6.20
m-CF_3	H	37.19	2.67	37.03	2.68
m-F	H	40.93	3.43	40.96	3.42
m-CH_3O	H	44.69	4.82	43.53	4.85

structure.[14] Therefore, an increase in the P—O bond order produced an upfield shift in the phosphorus resonance signal.

The P-31 chemical shifts of the two *ortho*-substituted phosphonic dichlorides were shielded as compared to that of the *meta* and *para* isomers. The P-31 chemical shift of *o*-tolylphosphonic dichloride was shielded slightly ($\simeq$ 1.0 ppm). This shielding effect has been attributed to steric compression.[15,16] The magnitude of this gamma effect is small as anticipated by the results of Grim and Yankowsky.[12] On the other hand, the P-31 chemical shift of *ortho*-anisylphosphonic dichloride was shielded substantially ($\simeq$5.2 ppm) in comparison to that of the *meta* and *para* isomers. Shielding of the phosphorus nucleus by the lone electron pairs on oxygen might account for such a large gamma effect on a 4-coordinated phosphorus compound.[12]

EXPERIMENTAL

General. The proton NMR spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$ with TMS as an internal standard. The proton decoupled P-31 NMR spectra were recorded as $CDCl_3$ solutions with 85% H_3PO_4 as an external standard on a JEOL JNM-FX100 Fourier Transform NMR spectrometer at 40.3 MHz using an external lock. The FID was accumulated after a pulse width of 3 *μ sec* (23°C flip angle) and a pulse repetition of 1 *sec* using 16K data points and 16K zero filling points. Elemental analyses of new phosphonic acid derivatives[3] were within ±3% of the calculated value. These analyses were performed by Industrial Testing Laboratories, Inc., St. Louis, Mo. The phosphonous dichlorides were prepared according to the procedures described in the literature[6–9] as illustrated in Table III.

Method I. General Procedure for the Preparation of Diethyl Arylphosphonates

This procedure is essentially that described by Tavs.[2] A mechanically stirred mixture of the aryl halide (1 equiv) and anhydrous $NiCl_2$ (5 mol %)[17] was heated to 180°C under a static N_2 atm. Triethyl phosphite (1.2 equiv) was then added dropwise from a constant pressure dropping funnel. The ethyl halide was collected in a dry ice cooled flask. After the addition the mixture was heated at 180°C for an additional 1/2 hr. The mixture was then partitioned between CH_2Cl_2 and 5% aq HCl. The CH_2Cl_2 layer was washed with H_2O, dried ($MgSO_4$) and concentrated *in vacuo* to yield the crude phosphonate ester. Bulb to bulb distillation at 80°C (0.1 to 0.5 torr) removed the low boiling impurities.

Finally, bulb to bulb distillation of the remaining oil (see Table I) yielded pure phosphonate diester.

Method II. Diethyl meta-trifluoromethylphenylphosphonate

This procedure is representative of the preparation of diethyl arylphosphonates by this method and is a modification of that reported by Botts and co-workers.[4]

The Grignard reagent of *meta*-trifluoromethylphenyl bromide was prepared according to that described by Simons and Ramler[5] starting with 12.5 g (0.515 mol) of magnesium, 112.5 g (0.5 mol) of *meta*-bromobenzotrifluoride in 280 mL of anhydrous ether. The dark green Grignard solution was transferred to a 500 mL constant addition funnel under N_2 pressure using a double-ended needle.

The Grignard reagent was then added dropwise to a stirred solution of freshly distilled chlorophosphate (172.55 g, 1 mol) in 500 mL of anhydrous ether at −76°C. After the addition ($1\frac{1}{2}$ hr) the mixture was stirred at ambient temperatures for $1\frac{1}{2}$ hr and then poured into 300 mL of 5% HCl. The ether layer was washed with H_2O (3 × 500 mL), dried ($MgSO_4$) and concentrated *in vacuo* to yield an orange oil. Fractional distillation yielded the desired ester as a colorless oil (131.15 g; 93%) at 100–105°C and 0.6–0.9 torr.

Anal. Calcd for $C_{11}H_{14}F_3O_3P$: C, 46.82; H, 5.00. Found: C, 46.84; H, 4.99.

Preparation of Phosphonic Dichlorides with PCl_5

The magnetically stirred diethyl arylphosphonate (0.1 equiv) was treated portionwise with PCl_5(0.1 equiv). The homogeneous mixture was treated in one portion with additional PCl_5 (0.12 equiv) and the mixture was heated at reflux overnight. $POCl_3$ was removed on a rotary evaporator under vacuum and bulb to bulb distillation under high vacuum yielded the pure phosphonic dichloride in 90–95% yields.

General Procedure for the Hydrolysis of Phosphonate Esters

A magnetically stirred suspension of the ester (0.1 mol) in 100 mL of conc HCl was heated at reflux for 6–8 hr and then allowed to stand at ambient temperatures overnight. Suction filtration then yielded the phosphonic acids which were dried under an infrared lamp. Occasionally, the phosphonic acids did not precipitate. In that case, the solution was concentrated *in vacuo* and the resulting solid slurried in petroleum ether and suction filtered. In general, arylphosphonic acids can be recrystallized from ethyl acetate-petroleum ether mixtures. Other pertinent data are listed in Table II.

General Procedure for the Preparation of Phosphonic Dichlorides with Thionyl Chloride

The phosphonic acid (0.1 mol) was added portionwise to 100 mL of thionyl chloride which is heated at 55–60°C and contains 0.1 mL of DMF. After the addition, the mixture is heated at 55–60°C overnight. The excess thionyl chloride is removed on a rotary evaporator. Kugelrohr distillation under reduced pressure then yielded pure phosphonic dichloride in yields ranging from 90–95%.

DMSO Oxidation of Phosphorus Dichlorides

This procedure is a slight modification of that described by Amonoo–Niezer and co-workers[10] and is representative of this type of oxidation.

At −76°C and under a $CaSo_4$ drying tube, a magnetically stirred solution of *para*-fluorophenylphosphonous dichloride[6] (79 g, 0.4 mol) in 300 mL of CH_2Cl_2 was treated dropwise with a solution of DMSO (33 g, 0.423 mol) in 75 mL of CH_2Cl_2. After stirring at −76°C for an additional $\frac{1}{2}$ hr, the solution was allowed to equilibrate to ambient temperature. Concentration in vacuum yielded an oil which was distilled in a Kugelrohr at 140°C and 0.5 torr to yield a colorless oil (71.0 g, 84%). The P-31 signal is recorded in Table III.

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