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A General Route to Methoxy-Substituted Arylphosphonous Dichlorides *via* Mild Lewis Acid Catalysts

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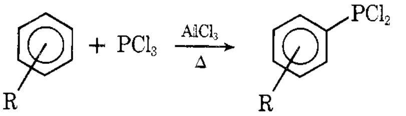
Treatment of anisoles **3** with phosphorus trichloride in the presence of catalytic amounts of anhydrous stannic chloride provides a convenient route to a variety of methoxy-substituted arylphosphonous dichlorides. Stannic chloride has been proven superior as a Friedel–Crafts catalyst for this reaction as compared to the previously reported use of aluminum chloride, ferric chloride, or zinc chloride. Substituent directive effects of polysubstituted anisoles have also been investigated.

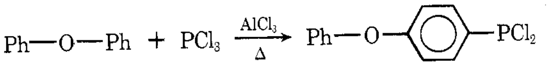
The introduction of the phosphonous dichloride moiety (PCl_2) into aromatic rings has been a topic of study for nearly 100 years.[1] Despite improvements in isolation and purification procedures, the Friedel–Crafts reaction of phosphorus trichloride with aromatic rings in the presence of an aluminum chloride catalyst remains a difficult, time-consuming, poor yield process[2] (eq 1). In cases where the aromatic ring is substituted by an ortho–para-directing group (alkyl, halogen, etc.), the reaction proceeds to yield the corresponding arylphosphonous dichloride, although the ortho–para-product ratios for substitution have been suspect due to lack of vigorous spectral methods of identification.[3]

In contrast, where the aromatic ring is substituted by a meta-directing group (NO_2, C(=O)R, etc.), the reaction fails completely; where the ring is substituted by a strongly activating group (NR_2), no catalyst is required.[4]



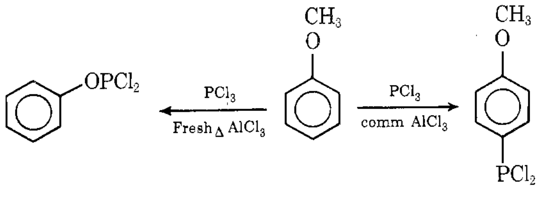
(1)

In cases where the aromatic ring is activated by OR, the overall reaction scheme is less well-defined. The reaction of diaryl ethers with phosphorus trichloride in the presence of aluminum chloride gives the para-substituted phosphonous dichlorides[5] (no ortho substitution found) (eq 2).



(2)

Where the reactant has been an *alkyl aryl* ether, however, the literature gives conflicting results. Michaelis[6] and Kunz[7] both reported that anisole, upon treatment with phosphorus trichloride and so-called "commercial" aluminum chloride, affords *p*-anisylphosphonous dichloride. Repetition of the reaction with freshly prepared aluminum chloride is reported to give the phenylphosphorodichloridite (eq 3).

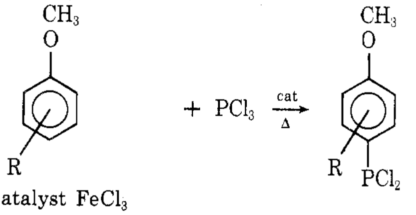


(3)

Other investigators have since found that this apparently straightforward reaction is useful for the preparation of *p*-anisylphosphonous dichloride.[8] In our hands, however, only the phosphorodichloridite (resulting from cleavage of the methyl ether followed by attack of phosphorus trichloride) could be isolated, despite repeated attempts with aluminum chloride.[9]

Clearly, a milder, more selective procedure for the introduction of the PCl_2 group into alkyl aryl ethers was desirable. The use of "deactivated" aluminum chloride (partially hydrated) was reviewed by Kosolapoff,[10] but no precise description of its preparation was given. Attempts to prepare $AlCl_3 \cdot X H_2O$ (by allowing anhydrous aluminum chloride to stand in air for several minutes up to several hours) gave a catalyst which was ineffective in the reaction under study (eq 3).

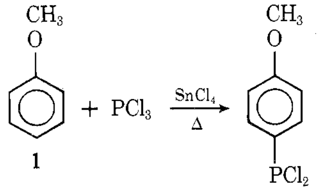
Since aluminum chloride is known to cleave alkyl aryl ethers,[11] a weaker Lewis acid catalyst was considered. Two reports of the use of zinc chloride[12] and ferric chloride[13] as catalysts for the reaction of anisoles with phosphorus trichloride have previously appeared, despite claims to the contrary.[14] However, neither author investigated the scope of the reaction. Poor yields, large amounts of undistillable residues, and formation of triaryl phosphines limited the use of these catalysts in preparation of arylphosphonous dichlorides to only two substrates, anisole[13] and 1,3-dimethoxybenzene[12,13] (eq 4).



(4)

R = H; catalyst $FeCl_3$
R = OCH_3; catalyst $ZnCl_2$

Both zinc chloride and ferric chloride give nonhomogeneous reaction mixtures, a fact which may contribute to isolation and purification problems. To avoid these difficulties, an alternative Friedel–Crafts catalyst was utilized. Stannic chloride[15] (anhydrous, organic soluble) in the presence of phosphorus trichloride and anisole **1** gave a 91% yield of phosphonous dichloride, no ether cleavage (and subsequent formation of phenylphosphorodichloridite), and a minimum of undistillable residue.[16,17]



1

2
(91%)

Table I
Phosphonous Dichlorides 4 from Anisoles 3

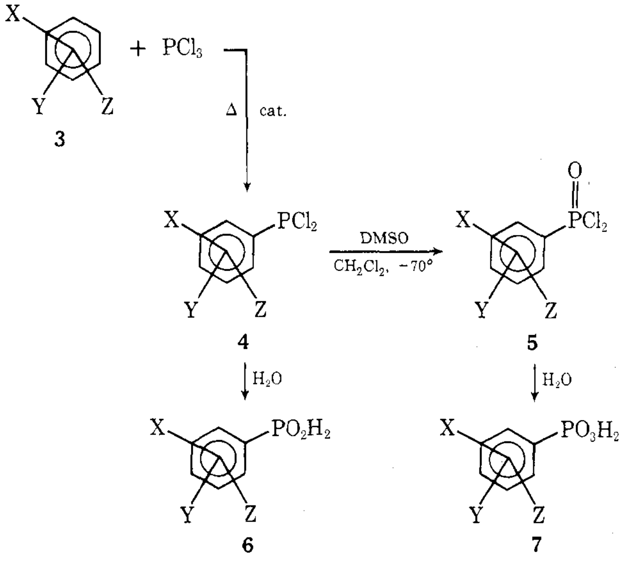
	Anisole							
Compd	X	Y	Z	Catalyst (rxn time)	Yield,[a] %	Phosphonous dichloride[b]	Bp, °C (mm)	Nmr (CCl_4 or $CDCl_3$)
3a	OCH_3	H	H	$SnCl_4$ (76 hr) $FeCl_3$ (44 hr)	91 31	4-$CH_3OC_6H_4$- (**4a**)	74–78 (0.05)[c]	3.78 (s, 3), 6.90 (dd, 2, *J* = 9 and 2 Hz), and 7.75 ppm (t, 2, *J* = 9 Hz)
3b	SCH_3	H	H	$SnCl_4$ (80 hr) $FeCl_3$ (60 hr)	36 19	4-$CH_3SC_6H_4$- (**4b**)	98–103 (0.02)	2.5 (s, 3), 7.15 (dd, 2, *J* = 9 and 2 Hz), and 7.7 ppm (t, 2, *J* = 9 Hz)
3c	OCH_3	2-CH_3	H	$SnCl_4$ (16 hr)	68	4-CH_3O-3-CH_3-C_6H_3- (**4c**)	103–106 (0.07)	2.3 (s, 3), 3.9 (s, 3), 6.8 (dd, 1, *J* = 9 and 2 Hz), and 7.5–7.9 ppm (m, 2)
3d	OCH_3	2-OCH_3	H	$SnCl_4$ (15 hr) $FeCl_3$ (24 hr)	26	3-CH_3O-4-CH_3O-C_6H_3- (**4d**)	112–115 (0.4)	3.75 (s, 3), 3.80 (s, 3), 6.8 (dd, 1, *J* = 9 and 2 Hz), and 7.0–7.5 ppm (m, 2)
3e	OCH_3	3-OCH_3	H	$FeCl_3$ (14 hr)	29	2-CH_3O-4-OCH_3-C_6H_3- (**4e**)	114–118 (0.05) mp 46–7[d]	3.80 (s, 3), 3.85 (s, 3), 6.3 (dd, 1, *J* = 4 and 2 Hz), 6.5 (dd, 1, *J* = 9.2 Hz), and 7.8 ppm (dd, 1, *J* = 10, 4 Hz)
3f	OCH_3	3-CH_3	H	$SnCl_4$ (49 hr)	71	4-CH_3O-2-CH_3-C_6H_3- and 4-CH_3-2-CH_3O-C_6H_3- (1:1) (**4f**)	93–97 (0.1)	2.4 (s, 3, 4-CH_3 isomer), 2.6 (d, 3, *J* = 3 Hz, 2-CH_3 isomer), 3.8 (s, 3, 2-CH_3 isomer), 3.9 (s, 3, 4-CH_3, isomer), 6.6–7.05 (m, 4), and 7.7–8.2 ppm (m, 2)
3g	OCH_3	2-OCH_3	4-OCH_3	$FeCl_3$ (40 hr)	26	2,4,5-CH_3O-C_6H_2- (**4g**)	136–140 (0.04)	3.9 (s, 9), 6.5 (d, 1, *J* = 6 Hz), and 7.48 (d, 1, *J* = 3 Hz)
3h	OCH_3	2-CH_3	3-CH_3	$SnCl_4$ (96 hr)	72	4-CH_3O-2,3-CH_3-C_6H_2- (**4h**)	108–111 (0.09)	2.1 (s, 3), 2.5 (s, 3), 3.8 (s, 3), 6.75 (d, 1, *J* = 9 Hz), and 7.88 ppm (dd, 1, *J* = 9 and 3 Hz)
3i	OCH_3	2-CH_3	4-CH_3	$SnCl_4$ (40 hr) $FeCl_3$ (60 hr)	50	2-CH_3O-3,5-CH_3-C_6H_2- (**4i**)	110–120 (0.05)	2.35 (s, 6), 3.9 (s, 3), 6.7 (d, 1, *J* = 6 Hz), and 7.6 ppm (d, 1, *J* = 4 Hz)
3j	OCH_3	2-CH_3	3-OCH_3	$SnCl_4$ (72 hr)	31	2,4-CH_3O-3-CH_3-C_6H_2- (**4j**)	128–137 (0.4)	2.15 (s, 3), 3.8 (s, 6), 6.75 (d, 1, *J* = 8 Hz), and 7.75 ppm (dd, 1, *J* = 8 and 3 Hz)
3k	OCH_3	3-C_2H_5	H	$SnCl_4$ (85 hr)	71	4-CH_3O-2-C_2H_5-C_6H_3- and 2-CH_3O-4-C_2H_5-C_6H_3 (1:1) (**4k**)	94–100 (0.1)	1.0–1.4 (m, 6), 2.3–3.2 (m, 4), 3.7 (s, 3), 3.8 (s, 3), 6.5–7.0 (m, 4), 7.6–8.1 (m, 2)

Table I
(Continued)

	Anisole							
Compd	X	Y	Z	Catalyst (rxn time)	Yield,[a] %	Phosphonous dichloride[b]	Bp, °C (mm)	Nmr (CCl_4 or $CDCl_3$)
3l	OCH_3	3-$(CH_3)_2CH$	H	$SnCl_4$ (148 hr)	55	4-CH_3O-2-$(CH_3)_2CH$-C_6H_3- and 2-CH_3O-4-$(CH_3)_2CH$-C_6H_3- (1:3) (**4l**)[e]	95–96 (0.05)	1.0–1.4 (m, 12), 2.6–3.2 (m, 2), 3.8 (s, 3), 3.9 (s, 3), 6.7–7.1 (m, 4), and 7.7–8.2 (m, 2)
3m	OCH_3	3-$(CH_3)_3C$-	H	$SnCl_4$ (88 hr)	26	2-CH_3O-4-$(CH_3)_3C$-C_6H_3- (**4m**)	103–110 (0.10)	1.3 (s, 9), 3.9 (s, 3), 6.8, 7.3 (m, 2), and 7.8 ppm (dd, 1, J = 8 and 4 Hz)
3n	O-n-C_4H_9	H	H	$SnCl_4$ (114 hr)	72	4-n-C_4H_9O-C_6H_4- (**4n**)	107–110 (0.10)	0.8–2.0 (m, 7), 4.0 (t, 2, J = 7 Hz), 7.0 (dd, 2, J = 9.2 Hz), and 7.9 ppm (t, 2, J = 9 Hz)
3o	OC_2H_5	H	H	$FeCl_3$ (133 hr)	55	4-C_2H_5O-C_6H_4- (**4o**)	78–87 (0.10)[f]	1.4 (t, 3, J = 7 Hz), 4.05 (q, 4, J = 7 Hz), 7.0 (dd, 2, J = 9.1 Hz), and 7.8 ppm (t, 2, J = 9 Hz)
3p	O-n-C_3H_7	H	H	$SnCl_4$ (90 hr)	72	4-n-C_3H_7O-C_6H_4- (**4p**)	92.8 (0.10)	1.0 (t, 3, J = 7 Hz), 1.8 (sextet, 2, J = 7 Hz), 3.9 (t, 2, J = 7 Hz), 7.0 (dd, 2, J = 9.2 Hz), and 7.8 ppm (t, 2, J = 9 Hz)

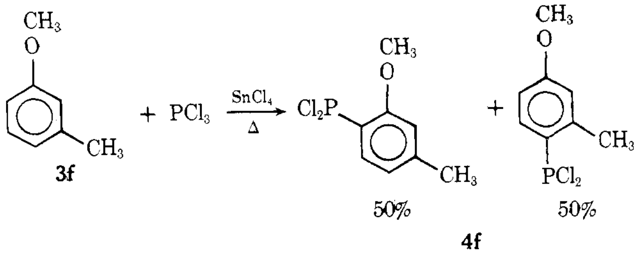
[a] Figure refers to distilled, pure material. [b] Satisfactory elemental analyses (±9.3%) were obtained for all new compounds. [c] Lit.[8] bp 140-141° (11 mm). [d] Lit.[13] bp 175-180° (12-15 mm). [e] Careful distillation effected separation of the isomer present in larger amount; nmr of 2-CH_3O-4-$(CH_3)_2CH$-C_6H_3-: 1.35 (d, 6, J = 7 Hz), 2.95 (sextet, 1, J = 7 Hz), 3.9 (s, 3). [f] Lit.[23] bp 266°.

This reaction has been extended to include a variety of substituted anisoles Table I). In several cases, ferric chloride was also used as the catalyst for comparative purposes. Structures of the phosphonous dichlorides were readily determined from the nmr spectra,[18] combustion analyses, and conversion[19] to the corresponding phosphonic dichlorides **5**, phosphinic acids **6**, and hydrolysis of the phosphonic dichlorides to the free phosphonic acids **7** (Table II).



An examination of the directive effects of the methoxyl groups suggests a logical pattern for electrophilic attack by phosphorus trichloride on the ring. The parent anisole **3a** gives only substitution para to methoxyl. No ortho substitution has been observed.[20] A similar result is obtained with o-methylanisole (**3c**). Introduction of the phosphonous dichloride moiety occurs only para to the methoxyl group. No substitution is seen at the positions ortho to methoxyl or para to methyl.[21]

In contrast, m-methylanisole (**3f**) undergoes reaction at both the positions ortho and para to methoxyl (para and ortho to methyl, respectively) in approximately equal amounts.



This suggests that the meta-methyl group may be hindering attack ortho to methyl by the rather bulky electro-

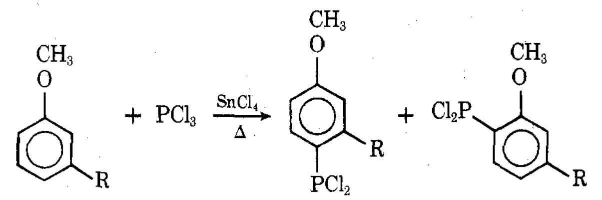
Table II
Phosphinic Acids 6 and Phosphonic Acids 7 from Phosphonous Dichlorides 4

Phosphonous dichloride 4	Phosphonic acid[a] 6	mp, °C 7	Nmr (DMSO-d_6) of phosphonic acid
4a	112–114[b] **6a**	168–169[c] **7a**	3.70 (s, 3), 6.95 (dd, 2, J = 9 and 3 Hz), 7.68 (dd, 2, J = 13 and 9 Hz), and 10.8 ppm (s, 2, position variable)
4b	105–106 **6b**	168–169 **7b**	2.6 (s, 3), 7.3–8.0 (m, 4), and 11.0 ppm (position variable)
4c	68–70 **6c**	183–184 **7c**	2.2 (s, 3), 3.8 (s, 3), 7.0 (dd, 1, J = 9 and 3 Hz), 7.55 (ddd, 1, J = 12, 9, and 1.5 Hz), 7.50 (dd, 1, J = 12 and 2 Hz), and 10 ppm (s, 2, position variable)
4d	138–139 **6d**	**7d**	3.75 (s, 6), 6.9–7.5 (m, 3), 10.3 (s, 1, position variable), and 7.5 ppm (d, 1, J = 540 Hz)[d]
4e	147–148[e] **6e**	163–163.5[f] **7e**	2.7 (s, 6), 6.4–6.7 (m, 2), 7.55 (dd, 1, J = 16 and 9 Hz), and 10.5 ppm (s, 2, position variable)
4f	108–108.5[g] 154–155[i] **6f**	185–186[h] 160–161[j] **7f**	2.55 (s, 3), 3.90 (s, 3), 6.75–7.0 (m, 2), 7.8 (dd, 1, J = 16 and 9 Hz) and 9.6 ppm (s, 2); 2.3 (s, 3), 3.75 (s, 3), 6.6–7.0 (m, 2), 7.5 (dd, 1, J = 15 and 8 Hz), and 10.6 ppm (s, 2)[k]
4g			
4h	141–142 **6h**	167–168 **7h**	2.10 (s, 3), 2.47 (s, 3), 3.80 (s, 3), 6.80 (dd, 1, J = 9 and 3 Hz), 7.65 (dd, 1, J = 13 and 9 Hz), and 8.8 (s, 2, position variable)
4i	150–151 **6i**		
4j	140–141 **6j**	168 **7j**	2.0 (s, 3), 3.65 (s, 3), 3.75 (s, 3), 6.70 (dd, 1, J = 8 and 3 Hz), 7.5 (dd, 1, J = 14 and 8 Hz), and 8.4 ppm (s, 2, position variable)
4k			
4l			
4m	164–166 **6m**		1.4 (s, 9), 3.9 (s, 3), 7.0–7.2 (m, 2), 7.4–7.8 (m, 1), 8.0 (s, 1, position variable), and 7.7 ppm (d, 1, J = 545 Hz)[d]
4n			
4o	118[l]		

[a] Satisfactory elemental analyses (±0.3%) were obtained for all new compounds. [b] Lit.[23] mp 113–114°. [c] Lit.[23] mp 158°. *Anal.* Calcd for $C_7H_7O_4P$: C, 44.75; H, 4.78. Found: C, 44.67; H, 4.85. [d] Spectrum of phosphinic acid. [e] Lit.[12] mp 160–161°. *Anal.* Calcd for $C_8H_{11}O_4P$: C, 47.51; H, 5.44. Found: C, 47.74; H, 5.25. [f] Lit.[12] mp 165–166°. *Anal.* Calcd for $C_8H_{11}O_5$: C, 44.06; H, 5.05. Found: C, 44.31; H, 5.13. [g] Isomers could be fractionally crystallized apart; mp for 2-CH_3-4-CH_3O-$C_6H_3PO_2H_2$. *Anal.* Calcd for $C_8H_{11}O_3P$: C, 51.70; H, 5.92. Found: C, 51.65; H, 5.97. [h] Isomers could be fractionally crystallized apart; mp for 2-CH_3-4-CH_3O-$C_6H_3PO_3H_2$. *Anal.* Calcd for $C_8H_{11}O_4P$: C, 47.5; H, 5.44. Found: C, 47 44; H, 5.50. [i] Isomers could be fractionally crystallized apart; mp for 2-CH_3O-4-CH_3-$C_6H_3PO_2H_2$. *Anal.* Calcd for $C_8H_{11}O_3P$: C, 51.70; H, 5.92. Found: C, 51.65; H, 5.92. [j] Isomers could be fractionally crystallized apart; mp for 2-CH_3O-4-CH_3-$C_6H_3PO_3H_2$. *Anal.* Calcd for $C_8H_{11}O_4P$: C, 47.51; H, 5.44. Found: C, 47.46; H, 5.57. [k] Nmr spectra for 2-CH_3-4-CH_3O-$C_6H_3PO_3H_2$ and 2-CH_3O-4-CH_3-$C_6H_3PO_3H_2$, respectively. [l] Lit.[23] mp 115°.

phile (presumably $PCl_2^+SnCl_5^-$) sufficiently to force some reaction to the position ortho to methoxyl (para to methyl).

To study the influence of steric hindrance in this reaction, three other meta-substituted anisoles were subjected to the reaction conditions with results consistent with the increased hindrance at the meta position. Successively increased hindrance at the meta position eventually gives substitution *only ortho* to methoxyl as in **4m**.

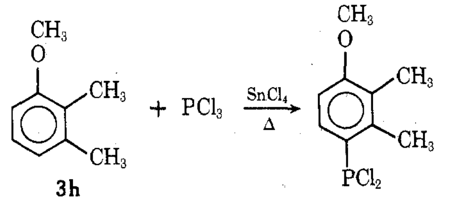


3k, R = Et **4k**, 50% 50%

l, R = *i*-Pr **l**, 24% 76%

m, R = *t*-Bu **m**, 0% 100%

An exception to this trend appeared, however, when 2,3-dimethylanisole was subjected to the reaction conditions. Based on analogy with **3f**, **3k**, **3l**, and **3m**, it was expected that approximately equal quantities of the two isomeric phosphonous dichlorides would be formed. Instead, only one isomer was formed, *i.e.*, the isomer with the phosphonous dichloride group para to methoxyl![22,23]



3h **4h**

The Friedel–Crafts procedure described herein provides a convenient method for the preparation of arylphosphonous dichlorides. A rational prediction of product distribution is also possible. The reaction appears reasonably general for methoxy-substituted aromatic rings which do not contain electron-withdrawing groups.

Experimental Section[24]

General Procedure for Preparation of Arylphosphonous Dichlorides. A. $SnCl_4$ Catalyst. A solution of 0.1 mol of the anisole, 0.30 mol (26 ml, 41 g) of phosphorus trichloride, and 2 ml of anhydrous stannic chloride was refluxed under dry nitrogen for the specified length of time. An extra 1–2 ml of stannic chloride was added every 12–18 hr. The mixture was concentrated under reduced pressure, and the residue was rapidly distilled at high vacuum. The clear oils obtained were redistilled slowly through a 10 in. Vigreux column. Separation of unreacted starting material (if present) and other low-boiling substances was effected near room temperature (0.05–0.3 mm). The desired product was collected at a much higher temperature [80–140° (0.05–0.3 mm)] and was sufficiently pure for elemental analysis.

B. $FeCl_3$ Catalyst. The same ratio of reactants as in (A) was used with 2.0 g of anhydrous ferric chloride instead of stannic chloride. Work-up consisted of filtration of the reaction mixture through Celite after the specified reaction time. The Celite was washed thoroughly with benzene, and the combined filtrates were concentrated under reduced pressure. The residue was vacuum distilled according to procedure A.

The phosphonous dichlorides were converted to the phosphonic acids by adaptation of the method of Amonoo-Nizer, Ray, Shaw, and Smith.[25]

A solution of 0.1 mol of the phosphonous dichloride in 200 ml of methylene chloride was cooled to −70° under nitrogen with mechanical stirring. A solution of 0.1 mol of dimethyl sulfoxide in 50 ml of methylene chloride was added dropwise at such a rate that the temperature remained below −50°. The solution was warmed to room temperature and then concentrated under reduced pressure to leave clear, slightly yellow oils or low-melting solids. These phosphonic dichlorides could be vacuum distilled or merely treated with enough acetone and water to solubilize the product. Heating the solution on the steam bath, followed by slow cooling, gave high (80–90%) overall yields of phosphonic acids. In cases where isomer mixtures were used, the slow rate of cooling was essential to isomer separation.

The phosphinic acids were prepared by treating 1–2 g of phosphonous dichloride with enough water (~10 ml) and acetone to provide a homogeneous solution. Heating the solution on the steam bath was followed by slow cooling to give 60–80% yields of phosphinic acids.

Registry No.—**3a**, 100-66-3; **3b**, 100-68-5; **3c**, 578-58-5; **3d**, 91-16-7; **3e**, 151-10-0; **3f**, 100-84-5; **3g**, 135-77-3; **3h**, 2944-49-2; **3i**, 6738-23-4; **3j**, 5673-07-4; **3k**, 10568-38-4; **3l**, 6380-20-7; **3m**, 33733-83-4; **3n**, 1126-79-0; **3o**, 103-73-1; **3p**, 622-85-5; **4a**, 19909-85-4; **4b**, 53534-47-7; **4c**, 53534-48-8; **4d**, 53534-49-9; **4e**, 53534-50-2; 4-CH_3O-**4f**, 53534-51-3; 2-CH_3O-**4f**, 53534-52-4; **4g**, 53534-53-5; **4h**, 53534-54-6; **4i**, 53534-55-7; **4j**, 53534-56-8; 4-CH_3O-**4k**, 53534-57-9; 2-CH_3O-**4k**, 53534-58-0; 4-CH_3O-**4l**, 53534-59-1; 2-CH_3O-**4l**, 53534-60-4; **4m**, 53534-61-5; **4n**, 53534-64-8; **4o**, 53534-62-6; **4p**, 53534-63-7; **6a**, 53534-65-9; **6b**, 53534-66-0; **6c**, 53534-67-1; **6d**, 53534-68-2; **6e**, 53534-69-3; 4-CH_3O-**6f**, 53534-70-6; 2-CH_3O-**6f**, 53534-71-7; **6h**, 53586-52-0; **6i**, 53534-72-8; **6j**, 53534-73-9; **6m**, 53534-74-0; **7a**, 21778-19-8; **7b**, 46061-42-1; **7c**, 53534-75-1; **7d**, 53534-76-2; **7e**, 53534-77-3; 4-CH_3O-**7f**, 53534-78-4; 2-CH_3O-**7f**, 53534-79-5; **7h**, 53534-80-8; **7j**, 53534-81-9; $SnCl_4$, 7646-78-8; $FeCl_3$, 7705-08-0; PCl_3, 7719-12-2.

References and Notes

(1) For a general literature review of the entire area of phosphonous dichloride chemistry, see G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds," Vol. 4, Wiley-Interscience, New York, N.Y., 1972, pp 75–157.

(2) A discussion of the improvements, limitations and problems in this process can be found in: G. M. Kosolapoff, "Friedel Crafts and Related Reactions," Vol. 4, G. Olah, Ed., Wiley-Interscience, New York, N.Y., 1965, pp 213; also see ref 1, p 79–81.

(3) G. M. Kosolapoff, ref 2, pp 222–224.

(4) M. Bourneuf, *Bull. Soc. Chem. Fr.*, **33**, 1808 (1923); L. Benda and. W. Schmidt, U.S. Patent 1607113 (1926); *Chem. Abstr.*, **21**, 249 (1927); H. Randnitz, *Ber.*, **60**, 743 (1927); M. P. Viout, *J. Rech. Cent. Nat. Rech.*, **No. 28**, 15 (1954); *Chem. Abstr.* **50**, 249 7077 (1956).

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(8) I. K. Jackson, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 2298 (1930); G. Kamai, *Zh. Obshch. Khim.*, **4**, 192 (1934).

(9) Varying the amounts of $AlCl_3$ had no effect on the outcome of the reaction. Use of a fresh bottle of anhydrous $AlCl_3$ likewise gave only ether cleavage.

(10) G. M. Kosolapoff, ref 2, p 223.

(11) H. S. Mason, *J. Amer. Chem. Soc.*, **69**, 2241 (1947); J. M. Bruce and F. K. Sutcliffe, *J. Chem. Soc.*, 4435 (1955); G. R. Pettit and D. M. Piatak, *J. Org. Chem.*, **25**, 721 (1960).

(12) I. S. Protopopov and M. Ya.Kraft, *Zh. Obshch. Khim.*, **34**, 1446 (1964); **33**, 3050 (1963).

(13) M. P. Viout, *J. Rech. Cent. Nat. Rech.*, **No. 28**, 15 (1954); M. P. Viout and P. Rumpf, *Bull. Soc. Chim. Fr.*, 768 (1957).

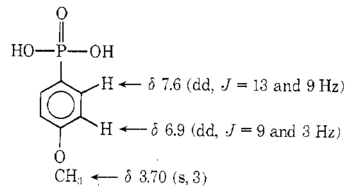
(14) G. M. Kosolapoff, ref 2, p 223.

(15) Stannic chloride has been used as a Friedel–Crafts catalyst for the preparation of 2-thienyl phosphonous dichloride but not for preparation of any benzenoid phosphonous dichlorides. See M. Bentov, L. David, and E. D. Bergman, *J. Chem. Soc.*, 4750 (1963).

(16) Reaction mixtures often precipitated some crystalline, hygroscopic complex, presumably ($SnCl_4$–PCl_3), which could be filtered off without difficulty before product isolation.

(17) In view of the utility of stannic chloride as a catalyst for the reaction under study, another mild, organic soluble catalyst candidate, titanium tetrachloride, was studied in one case. Using the same conditions as those used with stannic chloride, titanium tetrachloride was found to catalyze the conversion of anisole **3a** to *p*-anisyl phosphonous dichloride **4a** in approximately 50% yield after a reaction time of 64 hr.

(18) The nmr spectra of the phosphonous dichlorides, phosphinic acids, and phosphonic acids prepared were very diagnostic in determining patterns of substitution. The $-PCl_2$, $-PO_2H_2$, and $-PO_3H_2$ groups are all strongly deshielding, and protons ortho to them were found between δ 7.5 and 8.0, a full ppm lower field than protons ortho to methoxyl, methyl, or hydrogen. Coupling constants between ring protons and phosphorus did not follow a consistent pattern, apparently altered by steric and electronic factors; however, coupling between ortho and meta protons and phosphorus was routinely observed. No coupling between para protons and phosphorus could be seen. Proton–proton ring coupling constants were normal, 8–10 Hz for ortho and 1–3 Hz for meta. For example, *p*-anisylphosphonic acid gave a completely interpretable spectrum.



(19) E. H. Amonoo-Nizer, S. K. Ray, R. A. Shaw, and B. B. Smith, *J. Chem. Soc.*, 4296 (1965).

(20) Although unusual in aromatic electrophilic substitutions, complete specificity for para substitution is known. The Friedel–Crafts acetylation of anisole with aluminum chloride has been shown to give exclusively para substitution. See L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 61 (1963).

(21) In addition, *p*-dimethoxybenzene or *p*-methylanisole both failed to react under the reaction conditions.

(22) That the isomer formed was correctly identified was shown by comparison of its nmr spectrum with that of the isomeric mixtures of phosphonous dichlorides from *m*-methylanisole, *m*-isopropylanisole, and the single isomer obtained from *m-tert*-butylanisole.

(23) A further unexpected result came from the observation that 1,2,3-trimethoxybenzene failed to react at all under the conditions employed, while 3-methyl veratrole gave primarily ether cleavage to the aryl di-$OPCl_2$ product. A rationale for the abnormal reactivities of certain anisoles studied is not clear. However, it probably involves steric inhibition of resonance in the polysubstituted anisoles, especially those in which ring substituents are in consecutive positions. See, for instance, L. M. Stock, "Aromatic Substitution Reactions," K. L. Rinehart, Ed., Prentice-Hall, Englewood Cliffs, N.J. 1968, pp 54–55.

(24) Nmr spectra were recorded on a Varian Model T-60 or EM-360 spectrometer in CCl_4 or $CDCl_3$ for the phosphonous dichlorides and DMSO-d_6 for the phosphinic and phosphonic acids with tetramethylsilane (TMS) as the internal standard. The chemical shifts are reported in ppm (δ). All boiling points and melting points are uncorrected. Melting points were determined on a Mel-Temp apparatus. Elemental analyses were determined by Atlantic Microlabs, Atlanta, Georgia. Most of the anisoles were commercially available. Those that were not were prepared by alkylation of the corresponding phenols according to the procedure of G. N. Vyas and N. M. Shah, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 837.

(25) E. H. Amonoo-Nizer, S. K. Ray, R. A. Shaw, and B. B. Smith, *J. Chem. Soc.*, 4296 (1965).