

SYNTHESIS OF ARYL- AND HETARYLPHOSPHONATES

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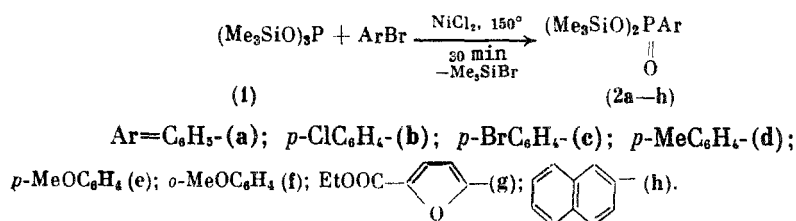
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The reaction of tris(trimethylsilyl) phosphite with aryl or hetaryl halides under homogeneous catalysis conditions gave bis(trimethylsilyl)phosphonates. Treatment of these products with methanol gave the corresponding aryl- or hetarylphosphonic acids in quantitative yield.

Keywords: tris(trimethylsilyl) phosphite, aryl and hetaryl halides, homogeneous catalysis, bis(trimethylsilyl)phosphonates, arylphosphonic acids.

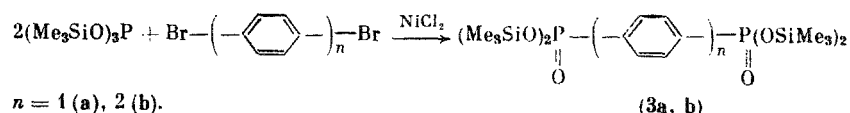
The use of nickel or palladium complex catalysts enables us to obtain dialkyl arylphosphonates in high yield by the cross-coupling of aryl chlorides or aryl bromides with trialkyl phosphites [1, 2]. Subsequent hydrolysis of these compounds leads to the formation of arylphosphonic acids [3].

We have shown that tris(trimethylsilyl) phosphite (1) is a convenient starting reagent for the preparation of dialkyl arylphosphonates or arylphosphonic acids. The cross-coupling of 1 with aryl bromides catalyzed by nickel chloride is much faster than with trialkyl phosphites and is complete in 20-30 min at 150°C. The arylphosphonate yield is 90-98%.



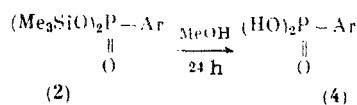
Aryl bromides with both electron-withdrawing or electron-donating substituents, α -naphthyl bromide, and hetaryl bromides were used in this reaction. The presence of *ortho* substituents in the benzene ring of the aryl bromide does not decrease the yield of the cross-coupling products.

The same high yields were obtained when two phosphonate groups were introduced into the benzene ring in the reaction of silyl phosphite (1) with 1,4-dibromobenzene and 1,4-dibromodiphenyl.



All these compounds were characterized by the physicochemical indices, elemental analysis, and ^{31}P NMR spectroscopy (Table 1).

Treatment of these products with methanol at room temperature leads to the formation of arylphosphonic acids (4) in quantitative yield. We should note that saponification may be carried out *in situ*, i.e., without prior isolation of the arylphosphonates.



Similar cross-coupling reactions of tris(trimethylsilyl) phosphite were carried out with perfluoropyridine (5a), perchloropyridine (5b), and 3-cyanotetrachloropyridine (5c). Pentahalopyridines are known to react with trialkyl phosphites without a catalyst to give the corresponding phosphonates. However, these reactions require prolonged heating, proceed without selectivity, and the yield of the monosubstitution products is not more than 50% [4].

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TABLE 1. Indices for Aryl- and Hetarylphosphonates 2 and 3

Com- pound	Yield, %	Bp, °C (p, torr)	³¹ P NMR spectrum, δ, ppm	Found Calculated, %			Chemical formula
				C	H	P	
2a	98	98(1)	0.73	47.66	7.62	10.24	C ₁₂ H ₂₃ PO ₃ Si ₂
2b	90	100(1)	1.0	47.68	7.62	10.23	
2c	90	116(1)	-2.95	42.77	6.55	9.20	C ₁₂ H ₂₂ PO ₃ Si ₂ Cl
				42.73	6.55	9.30	
2d	98	112(1)	0.83	41.23	6.27	8.90	C ₁₂ H ₂₂ PO ₃ Si ₂ Br
				40.80	6.27	8.77	
2e	98	110(1)	0.16	49.43	7.96	9.84	C ₁₃ H ₂₅ PO ₃ Si ₂
				49.32	7.96	9.83	
2f	92	105(0.7)	0.20	46.99	7.60	9.51	C ₁₃ H ₂₅ PO ₄ Si ₂
				46.99	7.66	9.38	
2g *	93		-21.0	46.90	7.63	9.41	C ₁₃ H ₂₅ PO ₄ Si ₂
2h	90	126(0.5)	-0.35	46.99	7.66	9.38	
3a *	92	†	-20.0	54.57	7.55	8.84	C ₁₆ H ₂₅ PO ₃ Si ₂
3b *	90	†	-19.0	54.55	7.55	8.84	

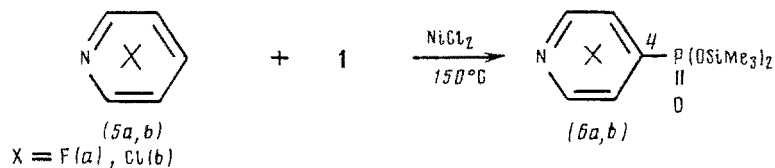
*The corresponding phosphonic and bisphosphonic acids were obtained without isolating the arylphosphonates by treating the reaction mixture with methanol.

†Decomposes upon distillation.

TABLE 2. Characteristics of Pyridylphosphonates (6a)-(6c)

Com- pound	Yield, %	Bp, °C (p, torr)	³¹ P NMR spec- trum, δ, ppm	¹³ C NMR spectrum, δ, ppm					
				C ²	C ³	C ⁴	C ⁵	C ⁶	C≡N
6a	99	184(0.03)	-15.0						
6b	99	196(0.02)	-14.0	148.7	132.6	140.2	132.6	148.7	-
6c	99	205(0.03)	-14.7	149.3	112.8	141.2	132.8	148.6	112.0

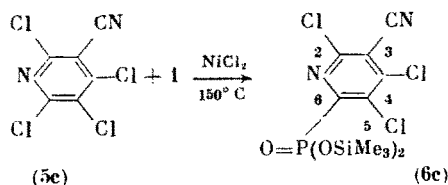
We have found that substituted pyridines (5a)-(5c) react readily with tris(trimethylsilyl) phosphite in the presence of catalytic amounts of nickel chloride to give the corresponding phosphonates in almost quantitative yield. This reaction proceeds under standard conditions at 150°C over 30 min.



We note that, under noncatalytic conditions, tris(trimethylsilyl) phosphite also reacts better than trialkyl phosphites. The yield of the final products is 60-69%.

The reaction of 1 with pentafluoro(chloro)pyridines proceeds with strict selectivity to give only one isomer, namely, 4-phosphorus-substituted pyridine (6a) and (6b).

The reaction of 1 with 5c also leads to the formation of only one product, namely, 6c.



All the hetarylphosphonates synthesized were characterized by their physicochemical indices as well as ¹³C and ³¹P NMR spectroscopy (Table 2). The structures of hetarylphosphonates (6a)-(6c) were established using literature data [5, 6].

EXPERIMENTAL

The ^{31}P NMR spectra were taken on Varian FT-80A and Jeol C-60HL spectrometers using 85% H_3PO_4 as the external standard. The ^{13}C NMR spectra were taken on a Varian FT-80A spectrometer in CDCl_3 relative to TMS.

Synthesis of Bis(trimethylsilyl) Aryl- and Hetarylphosphonates (2a)-(2h) (general procedure). A mixture of 0.1 mole tris(trimethylsilyl) phosphite, 0.1 mole aryl bromide, and 5 mole % anhydrous nickel chloride was maintained at 150°C for 20-30 min in a dry argon atmosphere. The reaction mixture was distilled in vacuum. The yields, physicochemical indices, ^{31}P NMR spectral data, and elemental analysis data for (2a)-(2h) are given in Table 1. The yields of (6a)-(6c) as well as the ^{13}C and ^{31}P NMR spectral data for these compounds are given in Table 2.

Arylphosphonic acids (4) (general procedure). A sample of 0.2-0.4 mole methanol was added to 0.1 mole arylphosphonate 2. The mixture was maintained for 24 h at about 20°C . Methanol was distilled off and the residue was recrystallized from water. The physical constants of products (4) corresponded to the literature data [7, 8].

REFERENCES

1. P. Tavs, *Chem. Ber.*, **103**, 242 (1970).
2. I. V. Berdnik, V. V. Sentemov, and E. A. Krasil'nikova, *Zh. Obshch. Khim.*, **56**, No. 1, 223 (1986).
3. Ch. Yuan and H. Feng, *Synthesis*, No. 2, 140 (1990).
4. W. Boenigh and G. Hagete, *Chem. Ber.*, **116**, 2418 (1983).
5. I. Collins and S. M. Roberts, *J. Chem. Soc., C*, No. 1, 167 (1971).
6. S. M. Roberts, *Chem. Commun.*, No. 17, 893 (1967).
7. A. Michaelis, *Liebigs Ann. Chem.*, **18**, 265 (1876).
8. A. Michaelis, *Liebigs Ann. Chem.*, **193** (1896).