

## LITERATURE CITED

1. F. K. Velichko, L. V. Balabanova, T. T. Vasil'eva, and A. B. Terent'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 1, 454 (1990).
2. R. Kh. Freidlina, F. K. Velichko, and A. B. Terent'ev, *Usp. Khim.*, 53, 370 (1984).
3. T. T. Vasil'eva, I. A. Fokina, S. V. Vitt, et al., *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1807 (1990).
4. T. T. Vasil'eva, R. G. Gasanov, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1290 (1979).
5. R. Kh. Freidlina, F. K. Velichko, S. S. Zlotskii, et al., *Radical Telomerization* [in Russian], Khimiya, Moscow (1988), p. 53.
6. N. V. Kruglova and N. A. Petrova, *Zh. Prikl. Khim.*, No. 7, 1660 (1987).
7. F. W. Grevels and E. Werner von Gustorf, *Liebigs Ann. Chem.*, No. 3, 547 (1975).
8. USSR Inventor's Certificate No. 393,264: *Byull. Izobret.*, No. 33, 89 (1973).

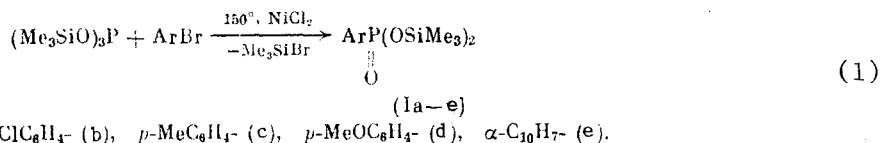
PREPARATION OF ARYLPHOSPHONATES BY THE REACTION OF ARYL  
HALIDES WITH TRIS(TRIMETHYLSILYL) PHOSPHITE UNDER  
HOMOGENEOUS CATALYSIS CONDITIONS

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The reaction of tris(trimethylsilyl) phosphite with aryl bromides under homogeneous catalysis conditions gives bis(trimethylsilyl)arylphosphonates. The desilylation of these phosphonate products with methanol leads to arylphosphonic acids.

We have shown that arylphosphonates (Ia)-(Ie) may be obtained in virtually quantitative yields by the cross coupling of aryl bromides and tris(trimethylsilyl) phosphite with nickel chloride as the catalyst. Reaction (1) proceeds much more rapidly than the corresponding reaction with trialkyl phosphite [1, 2]. Aryl chlorides do not react under these conditions.



Subsequent treatment of arylphosphonates (Ia)-(Ie) with methanol at -20°C readily provides the corresponding arylphosphonic acids (IIa)-(IIe) in 90-95% yield.



Phosphonic acids (IIa)-(IIe) may be obtained by treating phosphonates (Ia)-(Ie) with methanol without their prior isolation.

## EXPERIMENTAL

The <sup>31</sup>P NMR spectra were taken on Varian T80A and Jeol C-60H spectrometers with 85% H<sub>3</sub>PO<sub>4</sub> as the external standard.

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Bis(trimethylsilyl)phenylphosphonate (Ia) (general method). A mixture of 0.1 mole tris(trimethylsilyl) phosphite, 0.1 mole bromobenzene, and 5 mole % anhydrous nickel chloride was maintained for 30 min at 150°C in a dry argon atmosphere. The reaction mixture was distilled in vacuum to give 98% (Ia), bp 98°C (1 mm Hg).  $^{31}\text{P}$  NMR spectrum:  $\delta$  0.73 ppm. Found, %: C 47.66; H 7.62; P 10.24.  $\text{C}_{11}\text{H}_{23}\text{O}_3\text{PSi}_2$ . Calculated, %: C 47.68; H 7.62; P 10.23.

Bis(trimethylsilyl)-p-chlorophenylphosphonate (Ib) was obtained in 90% yield, bp 100°C (1 mm Hg).  $^{31}\text{P}$  NMR spectrum:  $\delta$  1.0 ppm. Found, %: C 42.77; H 6.55; P 9.20.  $\text{C}_{12}\text{H}_{22}\text{ClO}_3\text{PSi}_2$ . Calculated, %: C 42.73; H 6.55; P 9.20.

Bis(trimethylsilyl)-p-tolylphosphonate (Ic) was obtained in 98% yield, bp 112°C (1 mm Hg).  $^{31}\text{P}$  NMR spectrum:  $\delta$  0.83 ppm. Found, %: C 49.33; H 7.96; P 9.81.  $\text{C}_{13}\text{H}_{25}\text{O}_3\text{PSi}_2$ . Calculated, %: C 49.32; H 7.96; P 9.83.

Bis(trimethylsilyl)-p-methoxyphenylphosphonate (Id) was obtained in 98% yield, bp 110°C (1 mm Hg).  $^{31}\text{P}$  NMR spectrum:  $\delta$  0.16 ppm. Found, %: C 46.99; H 7.66; P 9.38.  $\text{C}_{13}\text{H}_{25}\text{O}_4\text{PSi}_2$ . Calculated, %: C 46.99; H 7.66; P 9.37.

Bis(trimethylsilyl)- $\alpha$ -naphthylphosphonate (Ie) was obtained in 90% yield, bp 126°C (0.5 mm Hg).  $^{31}\text{P}$  NMR spectrum:  $\delta$  0.35 ppm. Found, %: C 54.57; H 7.55; P 8.84.  $\text{C}_{16}\text{H}_{25}\text{O}_3\text{PSi}_2$ . Calculated, %: C 54.55; H 7.55; P 8.84.

Arylphosphonic Acids (IIa)-(IIe) (general method). A sample of 0.2 mole methanol was added to 0.1 mole bis(trimethylsilyl)arylphosphonate (Ia)-(Ie). The mixture was maintained for 24 h at -20°C. Methanol was distilled off. The crystalline residue was recrystallized from water. The indices of the resultant arylphosphonic acids (IIa)-(IIe) were in complete accord with the data of Michaelis [3, 4].

#### LITERATURE CITED

1. P. Tavs, Chem. Ber., 103, 2428 (1970).
2. E. A. Krasil'nikova, Zh. Org. Khim., 56, No. 11, 959 (1986).
3. A. Michaelis, Ber., 8, 499 (1875).
4. A. Michaelis, Liebigs Ann. Chem., 293, 193 (1896).