

## LETTERS TO THE EDITOR

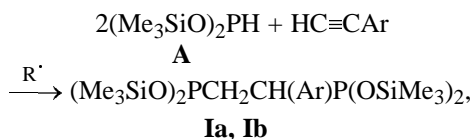
# Addition of Bis(trimethylsiloxy)phosphine to Aryl-substituted Acetylenes

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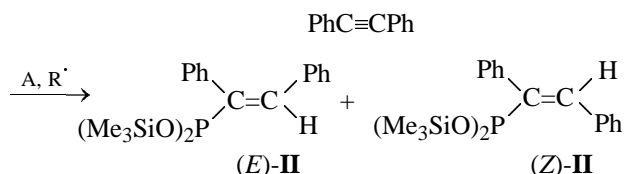
Received June 22, 2004

Addition of bis(trimethylsiloxy)phosphine to styrene, its heterocyclic analogs, and vinylferrocene is a convenient method for preparing functionalized phosphonites and their derivatives [1]. In the present work we showed that bis(trimethylsiloxy)phosphine **A** reacts with aryl-substituted acetylenes in a way much different from its exothermic addition to dimethyl acetylenedicarboxylate [2], i.e. by a radical mechanism and only in the presence of a catalyst, azodiisobutyronitrile, under conditions of its thermolysis at 100–120°C. Thus the reactions of phosphine **A** with phenyl- and anisylacetylenes involve double regioselective addition to the acetylene fragment to form diphosphonites **I**.



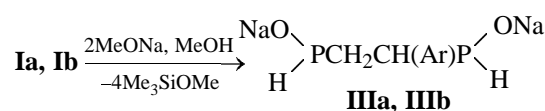
Ar = Ph (**a**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**b**).

Under the same conditions, the reaction of excess phosphine **A** with tolane stops on the formation of substituted vinylphosphonite **II** which, according to NMR data, is 2 : 1 mixture of the *E* and *Z* isomers.



Treatment of compounds **I** with dilute solutions of sodium methylate in methanol provides water-soluble salts as white hygroscopic crystals.

The NMR spectra of compounds **I–III** contain characteristic signals of the P<sup>1</sup>C<sup>1</sup>H<sub>2</sub>C<sup>2</sup>H(C<sup>3</sup>)P<sup>2</sup> and



Ar = Ph (**a**), 4-MeOC<sub>6</sub>H<sub>4</sub> (**b**).

PC<sup>1</sup>=C<sup>2</sup>H fragments, whose parameters are given below. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra, the proton and <sup>13</sup>C signals of the CH<sub>2</sub> fragment of compound **II** overlap with the respective signals of the phenyl fragments. For compound **II**, the NMR data for the preferred isomer are given first.

**1,2-Bis[bis(trimethylsiloxy)phosphino]-1-phenylethane (Ia).** A mixture of 42 g of bis(trimethylsiloxy)phosphine, 6.1 g of phenylacetylene, and 0.3 g of azodiisobutyronitrile was heated to 100°C, after which the temperature was raised to 130°C over the course of 1 h. Distillation gave 24.3 g (78%) of diphosphonite **Ia**, bp 133°C (0.5 mm Hg). <sup>1</sup>H NMR spectrum, δ, ppm: 1.85–2.0 m (C<sup>1</sup>H<sub>A</sub>H<sub>B</sub>), 2.84 m ABMX system [C<sup>2</sup>H<sub>M</sub>, <sup>2</sup>J(P<sup>2</sup>H<sub>M</sub>) 3.6, <sup>3</sup>J(H<sub>B</sub>H<sub>M</sub>) 11.6, <sup>3</sup>J(H<sub>B</sub>H<sub>M</sub>) 9.2 Hz]. <sup>13</sup>C NMR spectrum, δ<sub>C</sub>, ppm: 40.27 d.d (C<sup>1</sup>, <sup>1</sup>J<sub>PC</sub> 31.7, <sup>2</sup>J<sub>PC</sub> 15.5 Hz), 50.72 d.d (C<sup>2</sup>, <sup>1</sup>J<sub>PC</sub> 30.3, <sup>2</sup>J<sub>PC</sub> 9.6 Hz), 139.81 d.d (C<sup>3</sup>, <sup>2</sup>J<sub>PC</sub> 9.1, <sup>3</sup>J<sub>PC</sub> 3.1 Hz). <sup>31</sup>P NMR spectrum, δ<sub>P</sub>, ppm: 160.89 d (P<sup>1</sup>, <sup>3</sup>J<sub>PP</sub> 7.0 Hz), 148.94 d (P<sup>2</sup>, <sup>3</sup>J<sub>PP</sub> 7.0 Hz).

Compounds **Ic** and **II** were obtained analogously.

**1-Anisyl-1,2-bis[bis(trimethylsiloxy)phosphino]ethane (Ib).** Yield 74%, bp 139°C (0.5 mm Hg). <sup>1</sup>H NMR spectrum, δ, ppm: 1.85–2.05 m (C<sup>1</sup>H<sub>A</sub>H<sub>B</sub>), 2.80 m ABMX [C<sup>2</sup>H<sub>M</sub>, <sup>2</sup>J(P<sup>2</sup>H<sub>M</sub>) 4.0, <sup>3</sup>J(H<sub>A</sub>H<sub>M</sub>) 12.4, <sup>3</sup>J(H<sub>B</sub>H<sub>M</sub>) 8.6 Hz], 3.91 s (OCH<sub>3</sub>). <sup>13</sup>C NMR spectrum, δ<sub>C</sub>, ppm: 39.60 d (C<sup>1</sup>, <sup>1</sup>J<sub>PC</sub> 30.0, <sup>2</sup>J<sub>PC</sub> 14.9 Hz), 49.07 d.d (C<sup>2</sup>, <sup>1</sup>J<sub>PC</sub> 27.6, <sup>2</sup>J<sub>PC</sub> 11.3 Hz), 130.75 d.d (C<sup>3</sup>, <sup>2</sup>J<sub>PC</sub> 9.0, <sup>3</sup>J<sub>PC</sub> 3.4 Hz), 55.02 s (OCH<sub>3</sub>), 157.85 s

(OC=).  $^{31}\text{P}$  NMR spectrum,  $\delta_{\text{p}}$ , ppm: 164.33 d ( $\text{P}^1$ ,  $^3J_{\text{PP}}$  8.4 Hz), 151.46 d ( $\text{P}^2$ ,  $^3J_{\text{PP}}$  8.4 Hz).

**Bis(trimethylsilyl) (1,2-diphenylvinyl)phosphonite (II).** Yield 69%, bp 152°C (0.5 mm Hg).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 151.34 d ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  36.6 Hz) and 152.41 d ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  45.2 Hz), 1.57 d (CSi,  $^3J_{\text{PC}}$  3.2 Hz) and 1.45 d (CSi,  $^3J_{\text{PC}}$  2.9 Hz).  $^{31}\text{P}$  NMR spectrum,  $\delta_{\text{p}}$ , ppm: 144.26 and 139.99 s.

**1-Phenylethylenebis(sodium hydrogen phosphonite) (IIIa).** To a solution of 3.2 g of sodium methylate in 50 ml of methanol, a solution of 15.7 g of phosphonite **Ia** in 30 ml of diethyl ether was added with stirring at 10°C. The resulting mixture was heated to boiling, the solvent was removed, and the residue was kept in a vacuum (1 mm Hg) for 1 h to obtain 8.2 g (98%) of salt **IIIa**.  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 6.65 d ( $\text{P}^1\text{H}$ ,  $^1J_{\text{PH}}$  516.3 Hz), 6.78 d.d ( $\text{P}^2\text{H}$ ,  $^1J_{\text{PH}}$  515.5,  $^3J_{\text{HH}}$  2.4 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 29.66 d ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  89.5 Hz), 43.04 d ( $\text{C}^2$ ,  $^1J_{\text{PC}}$  82.9 Hz), 136.4–134.4 m ( $\text{C}^3$ ).  $^{31}\text{P}$  NMR spectrum,  $\delta_{\text{p}}$ , ppm: 29.06 d.d ( $\text{P}^1$ ,  $^1J_{\text{PH}}$  516.3,  $^3J_{\text{PP}}$  55.6 Hz), 23.56 d.d ( $\text{P}^2$ ,  $^1J_{\text{PH}}$  515.5,  $^3J_{\text{PP}}$  55.6 Hz). Found, %: C 34.43; H 3.69.  $\text{C}_8\text{H}_{10}\text{Na}_2\text{O}_4\text{P}_2$ . Calculated, %: C 34.55; H 3.62.

Salt **IIIb** was obtained analogously.

**1-Anisylethylenebis(sodium hydrogen phosphonite) (IIIb).** Yield 96%.  $^1\text{H}$  NMR spectrum,  $\delta$ ,

ppm: 6.52 d ( $\text{P}^1\text{H}$ ,  $^1J_{\text{PH}}$  519.4 Hz), 6.81 d.d ( $\text{P}^2\text{H}$ ,  $^1J_{\text{PH}}$  522.1,  $^3J_{\text{HH}}$  2.6 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 30.05 d ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  90.3 Hz), 41.89 d ( $\text{C}^2$ ,  $^1J_{\text{PC}}$  83.7 Hz), 135.1–135.3 m ( $\text{C}^3$ ), 54.92 s ( $\text{OCH}_3$ ), 158.01 s (OC=).  $^{31}\text{P}$  NMR spectrum,  $\delta_{\text{p}}$ , ppm: 35.83 d.d ( $\text{P}^1$ ,  $^1J_{\text{PH}}$  519.4,  $^3J_{\text{PP}}$  57.1 Hz), 29.55 d.d ( $\text{P}^2$ ,  $^1J_{\text{PH}}$  522.1,  $^3J_{\text{PP}}$  57.1 Hz). Found, %: C 34.94; H 3.98.  $\text{C}_9\text{H}_{12}\text{Na}_2\text{O}_5\text{P}_2$ . Calculated, %: C 35.08; H 3.92.

The NMR spectra were obtained on a Varian VXR-400 spectrometer in  $\text{CDCl}_3$  or  $\text{D}_2\text{O}$  (salts **III**) against TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or 85% of  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$  ( $^{31}\text{P}$ ).

## REFERENCES

1. Prishchenko, A.A., Livantsov, M.V., Livantsova, L.I., Novikova, O.P., and Grigor'ev, E.V., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 12, p. 2055; Prishchenko, A.A., Livantsov, M.V., Livantsova, L.I., Pol'shchikov, D.G., and Grigor'ev E.V., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 2, p. 346; Livantsova, L.I., Prishchenko, A.A., Livantsov, M.V., Nikolaev, S.N., and Grigor'ev, E.V., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 7, p. 1220; Livantsov, M.V., Prishchenko, A.A., Livantsova, L.I., Nikolaev, S.N., Meleshonkova, N.N., and Grigor'ev, E.V., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 1, p. 163.
2. Prishchenko, A.A., Livantsov, M.V., Livantsova, L.I., Grigor'ev, E.V., Goncharova, Zh.Yu., and Novikova, O.P., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 11, p. 1912.