Base-Catalyzed Addition of Phosphine to Aryl- and Hetarylethynes. An Efficient Method for the Preparation of 2-Substituted Trivinylphosphines

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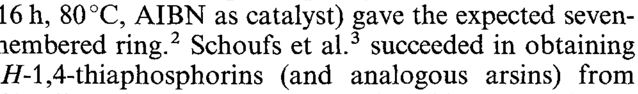
A number of *Z,Z,Z*-tris(1-alkenyl)phosphines **2** have been obtained in good yields from phosphine and acetylenes in the super-base system potassium hydroxide/hexamethylphosphoric triamide.

Only a few data are known about addition of phosphines to acetylenes. Addition of diphenylphosphine to acetylene was effected by heating the mixture for several days at 100 °C.[1a] Other examples of radical additions of phosphines to acetylenes have been reported by Rauhut[1b] and Lin.[1c] Addition of phenylphosphine to 1,5-hexadiyne (16 h, 80 °C, AIBN as catalyst) gave the expected seven-membered ring.[2] Schoufs et al.[3] succeeded in obtaining 4*H*-1,4-thiaphosphorins (and analogous arsins) from di(1-alkynyl) sulfides and phenylphosphine under the catalytic action of lithium amide in liquid ammonia. In a previous paper[4] we described the formation of tris(styryl)phosphine from red phosphorus, phenylacetylene and potassium hydroxide in hexamethylphosphoric triamide (HMPT). French investigators[5] recently mentioned the formation of this compound, using similar conditions.

Our present communication presents an efficient method for preparing *Z,Z,Z*-tris(alkenyl)phosphines **2** from aryl- and hetarylethynes and phosphine. This gas is introduced at atmospheric pressure into a mixture of potassium hydroxide, water and HMPT, while the acetylene is slowly added. 1-Pentyne was shown to be unreactive. We presume that the products **2** are formed through a series of nucleophilic additions of the intermediary phosphides (present in small equilibrium concentrations) to the triple bond. The *Z,Z,Z*-configuration of the double bonds in **2** is in agreement with a mechanism of *trans*-nucleophilic addition.



(2)

All attempts to isolate secondary phosphines (compare our previous paper[6] on the addition of phosphine to arylalkenes) under milder conditions (lower temperature, higher ratio of water and potassium hydroxide lower amounts of acetylenes) failed, tertiary phosphines being the only products.

Trivinylphosphines 2; General Procedure:

A 500-mL round-bottomed 3-necked flask was fitted with a gas inlet, combined with a pressure-equalizing dropping funnel, a gas-tight mechanical stirrer and a combination of outlet and thermometer. In the flask were placed red phosphorus (9 g) and dioxane (20 mL) and in the dropping funnel 50 % (by weight) aq solution of KOH (30 g). The flask was connected, via a washing bottle (containing paraffin oil) with a 250-mL 3-necked flask containing KOH (7 g), HMPT (35 mL) and H_2O (3 mL). This second flask was equipped with an efficient mechanical stirrer, a combination of gas inlet tube and a dropping funnel containing a mixture of the acetylene **1** (0.07 mol) and HMPT (5 mL), and a combination of gas outlet and a thermometer. The outlet of the flask was connected with another washing bottle containing paraffin oil. After all connections had been made gas-tight, the flasks were flushed with N_2. The contents of the first flask were heated to ~ 70 °C, those of the second flask to 55–60 °C. The flow of N_2 was then stopped and the addition (dropwise) of the KOH solution started. The rate of this addition was adjusted such that PH_3 was evolved at a rate of ~ 50 bubbles per min. 10 min after the evolution of PH_3 had begun, the addition of the acetylene/HMPT mixture was started. This addition was carried out over ~ 15 min. After all KOH solution had been added, the temperatures of the first and second flask were maintained for an additional 2.5 h at ~ 70 and ~ 60 °C, respectively. The flasks were then cooled to about 20 °C while N_2 (~ 500 mL/min) was passed through the flasks for 2 min. Water (150 mL) was added to the mixture in the second flask, after which five extractions with Et_2O (50 mL portions) were carried out. The combined ethereal extracts were washed five times with H_2O (degassed with N_2) (50 mL portions), dried (K_2CO_3) and concentrated in vacuo. In the case of R = 2-thienyl and 2-furyl a yellowish precipitate was formed upon dilution of the reaction mixture with H_2O. The solids were washed successively with H_2O, EtOH and hexane and subsequently dried in vacuum (< 1 Torr) (Table).

Table. Trivinylphosphines **2** Prepared

Product **2**[a] R	Yield[b] (%)	mp (°C) (n_D^{20})	^1H, ^{31}P NMR ($CDCl_3$)[c] δ	*J* (Hz)
Ph	70	oil (1.6761)	7.30 (m, 15H), 7.12 (dd, 3H), 6.26 (dd, 3H), *– 63.83*	$^3J_{H,H} = 12.68$, $^3J_{H,P} = 24.40$, $^2J_{H,P} = 1.22$
4-FC_6H_4	75	47–48	7.42 (m, 6H), 7.06 (dd, 3H), 6.91 (m, 6H), 6.20 (dd, 3H) *– 60.57*	$^3J_{H,H} = 12.61$, $^3J_{H,P} = 23.46$, $^2J_{H,P} = 1.13$
2-thienyl	78	111–112	7.32 (d, 3H), 7.25 (dd, 3H), 7.20 (d, 3H), 6.99 (m, 3H), 6.09 (dd, 3H)	$^3J_{H,H} = 12.30$, $^3J_{H,P} = 25.02$, $^2J_{H,P} = 0.91$
2-furyl	61	104–105	7.34 (d, 3H), 6.86 (dd, 3H), 6.63 (d, 3H), 6.40 (dd, 3H), 6.10 (dd, 3H), *– 45.31*	$^3J_{H,H} = 12.68$, $^3J_{H,P} = 23.17$ ($^2J_{H,P}$ was too small to be determined)

[a] All products have the *Z, Z, Z*-configuration (cf. Ref. 7 for assignments). Satisfactory microanalyses obtained: C ± 0.32, H ± 0.35, N ± 0.47 [Exception **2** (R = 2-furyl), H + 0.76].
[b] Yield based on acetylene.
[c] ^{31}P NMR values are given in italics.

(1) (a) Hoffmann, H.; Diehr, H.J. *Chem. Ber.* **1965**, *98*, 363.
(b) Rauhut, M.M.; Currier, W.A.; Semsel, A.M.; Wystrach, V.P. *J. Org. Chem.* **1961**, *26*, 5138.
(c) Lin, K.C. US Patent 3673285 (1972); *Chem. Abstr.* **1972**, *77*, 101890.

(2) Märkl, G.; Dannhardt, G. *Tetrahedron Lett.* **1973**, 1455.

(3) Schoufs, M.; Meijer, J.; Vermeer, P.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 241.

(4) Trofimov, B.A.; Gusarova, N.K.; Malysheva, S.F.; Rahhmatulina, T.N.; Voronkov, M.G.; Dimitriev, V.I.; Shaikhudinova, S.I. *Phosphorus, Sulfur Silicon Relat. Elen.* **1991**, *55*, 271.
Trofimov, B.A.; Gusarova, N.K.; Malysheva, S.F.; Rahhmatulina, T.N.; Lyavinets, A.S.; Voronkov, M.G. *Zh. Obshch. Khim.* **1991**, *61*, 1310; *Chem. Abstr.* **1992**, *116*, 21148.

(5) Semenzin, D.; Etemad-Moghadam, G.; Albouy, D.; Koenig, M. *Tetrahedron Lett.* **1994**, *35*, 3297.

(6) Trofimov, B.A.; Brandsma, L.; Arbuzova, S.N.; Malysheva, S.F.; Gusarova, N.K. *Tetrahedron Lett.* **1994**, *35*, 7647.

(7) Duncan, M.; Gallagher, M.J. *Org. Magn. Res.* **1981**, *15*, 37.