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Reaction of Secondary Phosphine Oxides with Acylacetylenes

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Abstract—Secondary phosphine oxides reacted with 1-alkanoyl-2-phenylacetylenes in chemoselective fashion under mild conditions (20°C, THF) in the absence of a catalyst (diphenylphosphine oxide) or in the presence of potassium hydroxide [bis(2-phenylethyl)phosphine oxide] to give 1-alkyl-1-diphenyl(or 2-phenylethyl)-phosphoryl-3-phenylprop-2-yn-1-ols in up to 96% yield. The reaction of diphenylphosphine oxide with 1-alkanoyl-2-phenylacetylenes in the system KOH–THF (20°C) afforded not only adducts at the carbonyl group but also products of double α,β-addition at the triple bond, 2,3-bis(diphenylphosphoryl)-3-phenylpropan-1-ones.

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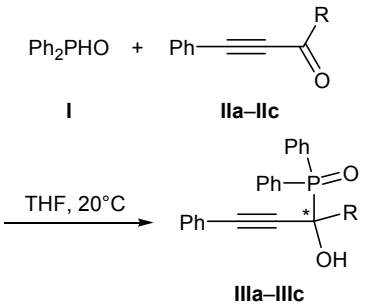
Tertiary phosphine oxides are key targets in the chemistry of organophosphorus compounds. They are widely used as ligands for metal complex catalysts [1–3], special solvents for stabilization of nanosystems in the synthesis of semiconductors [4], extractants for noble, rare-earth, and transuranium elements [5–7], fire-retardants [8], and photochromic [9] and luminescent materials [10]. Phosphine oxides are successfully used as building blocks, e.g., in the Wittig–Horner reaction [11–14], specifically, for the synthesis of substituted vitamin D_3 analogs [14]. Of particular interest are polyfunctionalized tertiary phosphine oxides; however, their synthesis involves some difficulties. A convenient synthetic approach to such compounds is based on the addition of secondary phosphine oxides to functionally substituted alkenes [15–18], alkynes [15, 17] (including α,β-acetylenic ketones [19]), aldehydes [20–24], and ketones [20, 21]. In the recent publication [25] we briefly reported on reactions of secondary phosphine oxides with 1-acetyl- and 1-butanoyl-2-phenylacetylenes in the system KOH–THF, which occurred in chemoselective fashion at the C=O group and led to the formation of functionalized tertiary phosphine oxides having a hydroxy group and an acetylenic fragment.

In the present work we performed a detailed study on nucleophilic addition of secondary phosphine oxides to bielectrophilic 1-alkanoyl-2-phenylacetylenes with a view to elucidate its chemo- and regioselectivity and efficiency, depending on the reactant structure and experimental conditions, as well as to develop a procedure for the synthesis of new polyfunctionalized tertiary phosphine oxides.

We have found that diphenylphosphine oxide (**I**) reacts with 1-alkanoyl-2-phenylacetylenes **IIa**–**IIc** under mild conditions in the absence of a catalyst (20°C, THF); the reaction is chemoselective, and the products are the corresponding adducts at the carbonyl group, (diphenylphosphoryl)phenylalkynols **IIIa**–**IIIc** (Scheme 1, Table 1). At an equimolar reactant ratio, the yield of **IIIa**–**IIIc** did not exceed 41% (Table 1; run nos. 1, 4, 6). The use of 2 equiv of diphenylphosphine oxide (**I**) allowed us to raise the yield of **IIIa**–**IIIc** to 65–96% (Table 1, run nos. 3, 5, 7). Increase in the yield of **IIIa**–**IIIc** in the presence of excess phos-

Scheme 1.



I **IIa–IIc** **IIIa–IIIc**

R = Me (**a**), Pr (**b**), *i*-Pr (**c**).

Table 1. Reaction of diphenylphosphine oxide (**I**) with acetylenic ketones **IIa**–**IIc**[a]

Run no.	R	Reactant ratio **I**:**II**	Reaction time, h	Yield of **III**,[b] %
1	Me	1:1	9	40 (**a**)
2[c]	Me	1:1	4	71 (**a**)
3	Me	2:1	9	96 (**a**)
4	Pr	1:1	35	41 (**b**)
5	Pr	2:1	35	77 (**b**)
6	*i*-Pr	1:1	35	13 (**c**)
7	*i*-Pr	2:1	35	65 (**c**)

[a] All reactions were carried out in THF at room temperature under argon.

[b] Calculated on the initial amount of **II**.

[c] The reaction was carried out with 10 mol % of KOH (with respect to **I**).

phine oxide **I** may be related to equilibrium character of the process [26] (see below).

As follows from the data in Table 1, the rate and efficiency of this reaction depend on the structure of the alkyl radical R in acetylenes **IIa**–**IIc**; their reactivity decreases in the series **IIa** > **IIb** > **IIc**, i.e., in parallel with increase in the degree of branching of the R radical. The yield of adduct **IIIa** increased almost twofold (simultaneously, the reaction time shortened more than twofold) when the reaction of diphenylphosphine oxide (**I**) with 1-acetyl-2-phenylacetylene (**IIa**) was carried out with equimolar amounts of the reactants in the presence of 10 mol % of KOH (Table 1; cf. run nos. 1 and 2). However, further increase in the amount of KOH resulted in reduced chemoselectivity of the process. The reactions of diphenylphosphine oxide (**I**) with equimolar amounts of acetylenes **IIa**–**IIc** in the presence of 20 mol % of KOH (20°C, THF) gave mixtures of adducts **IIIa**–**IIIc** and products of double α,β-addition at the triple bond, 2,3-bis(diphenylphosphoryl)-3-phenylpropan-1-ones **IVa**–**IVc** (Scheme 2; Table 2, run nos. 1–3) whose fraction increased in going from 1-acetyl-2-phenylacetylene **IIa** to acylacetylenes **IIb** and **IIc** having bulkier substituents (propyl and isopropyl groups, respectively) at the carbonyl carbon atom (Table 2, run nos. 1–3). We succeeded in obtaining compounds **IVa**–**IVc** as the major products using 2 equiv of phosphine oxide **I** with respect to acetylenic ketone **IIa**–**IIc** (Table 2, run nos. 4–6).

Table 2. Reaction of diphenylphosphine oxide (**I**) with acetylenic ketones **IIa**–**IIc** in the presence of 20 mol % of KOH (with respect to phosphine oxide **I**)[a]

Run no.	R	Reactant ratio **I**:**II**	Reaction time, h	Yield,[b] %	
				III	**IV**
1	Me	1:1	4	69 (**a**)	4 (**a**)
2	Pr	1:1	4	16 (**b**)	75 (**b**)
3	*i*-Pr	1:1	9	8 (**c**)	33 (**c**)
4	Me	2:1	4	36 (**a**)	37 (**a**)
5	Pr	2:1	4	Traces[d]	82 (**b**)
6	*i*-Pr	2:1	9	Not detected[d]	52 (**c**)
7[c]	Me	1:1	4	71 (**a**)	Not detected[d]

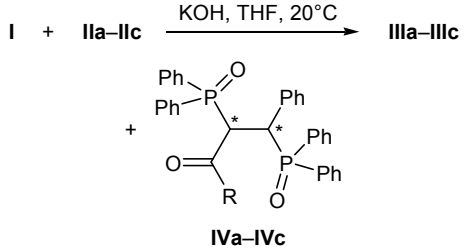
[a] All reactions were carried out in THF at room temperature under argon.

[b] Calculated on the initial amount of **II**.

[c] The reaction was carried out with 10 mol % of KOH (with respect to **I**).

[d] ^{31}P NMR monitoring.

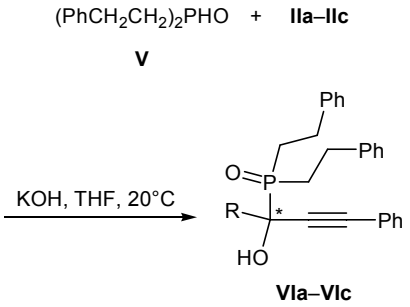
Scheme 2.



R = Me (**a**), Pr (**b**), *i*-Pr (**c**).

Unlike diphenylphosphine oxide (**I**), bis(2-phenylethyl)phosphine oxide (**V**) failed to react with 4-phenylbut-3-yn-2-one (**IIa**) in the absence of KOH (equimolar reactant ratio, 20°C, 9 h, THF; Table 3, run no. 1). The use of 2 equiv of phosphine oxide **V** with respect to acetylenic ketone **IIa** and prolonged contact of the reactants (20°C, 240 h, THF) led to formation of an insignificant amount of the adduct at the carbonyl group (compound **VIa**; Scheme 3; Table 3, run no. 2). On the other hand, in the presence of KOH (20°C, 35 h, THF) phosphine oxide **V** chemoselectively added to acetylenic ketones **IIa**–**IIc** to give acetylenic alcohols **VIa**–**VIc** in 67, 63, and 19% yield, respectively (Scheme 3; Table 3, run nos. 3–5). As in the reaction with diphenylphosphine oxide (**I**), acylacetylene **IIc** having an isopropyl group at the carbonyl carbon atom turned out to be least reactive toward bis(2-phenylethyl)phosphine oxide (**V**). Our results indicated

Scheme 3.

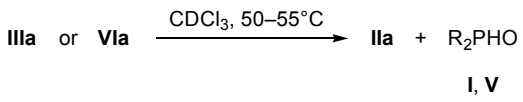


R = Me (**a**), Pr (**b**), *i*-Pr (**c**).

higher reactivity of diphenylphosphine oxide (**I**) compared to bis(2-phenylethyl)phosphine oxide (**V**); a probable reason is higher acidity of phosphine oxide **I** and hence higher concentration of diphenylphosphinite ions.

Tertiary phosphine oxides **IIIa**–**IIIc**, **IVa**–**IVc**, and **VIa**–**VIc** are crystalline substances that are stable at room temperature. However, adducts **IIIa** and **VIa** at the carbonyl group were shown (^{1}H, ^{13}C, and ^{31}P NMR monitoring) to undergo decomposition into initial acetylacetylene **IIa** and the corresponding phosphine oxide **I** or **V** on heating in $CDCl_3$ (50–55°C, 7–33 h; Scheme 4). The conversion of phosphine oxide **IIIa** was ~90% in 13 h, while the conversion of **VIa** was only ~15% over the same period of time. The observed decomposition of adducts **IIIa**–**IIIc** on heating in $CDCl_3$ and increase in their yield upon raising the concentration of one of the reactants (Table 1, run nos. 3, 5, 7) suggest equilibrium character of the process.

Scheme 4.



I, **IIIa**, R = Ph; **V**, **VIa**, R = $PhCH_2CH_2$.

Thus, we have developed a convenient, effective, chemoselective, and atom-economic synthesis of phosphorus-containing acetylenic alcohols via addition of secondary phosphine oxides at the carbonyl group of 1-acyl-2-phenylacetylenes. Under certain conditions the reaction with diphenylphosphine oxide may be directed toward predominant (or even exclusive) formation of 2,3-bis(diphenylphosphoryl)-3-phenylpropan-1-ones as a result of double α,β-addition at the triple bond. The newly synthesized polyfunctionalized tertiary phosphine oxides are promising as reactive building blocks for organic and organometallic synthesis and intermediate products for the design of specialty substances and materials.

Table 3. Reaction of bis(2-phenylethyl)phosphine oxide (**V**) with acetylenic ketones **IIa**–**IIc**[a]

Run no.	R	Amount of KOH, mol %	Reaction time, h	Reactant ratio **V**:**II**	Yield of **VI**,[b] %
1	Me	0	9	1:1	–[c]
2	Me	0	240	2:1	6[c] (**a**)
3	Me	20	35	1:1	67 (**a**)
4	Pr	20	35	1:1	63 (**b**)
5	*i*-Pr	20	35	1:1	19 (**c**)

[a] All reactions were carried out in THF at room temperature under argon.

[b] Calculated on the initial amount of **II**.

[c] ^{31}P NMR monitoring.

EXPERIMENTAL

The IR spectra were recorded in KBr on a Bruker IFS-25 spectrometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured from solutions in $CDCl_3$ on a Bruker DPX-400 instrument (400.13, 101.61, and 161.98 MHz, respectively); the chemical shifts were determined relative to hexamethyldisiloxane (^{1}H, ^{13}C) or 85% phosphoric acid (^{31}P). Signals in the NMR spectra were assigned using two-dimensional homo- and heteronuclear correlation techniques (HSQC, HMBC, NOESY).

Diphenylphosphine oxide (**I**) and bis(2-phenylethyl)phosphine oxide (**V**) were synthesized as reported in [27] and [28], respectively. Initial α,β-acetylenic ketones **IIa**–**IIc** were prepared from phenylacetylene and the corresponding aldehyde according to the procedure described in [29].

Tertiary phosphine oxides IIIa–IIIc (*general procedure***)** (Table 1, run nos. 3, 5, 7)**.** A solution of 1 mmol of diphenylphosphine oxide (**I**) and 0.5 mmol of acetylenic ketone **IIa**–**IIc** in 4 ml of THF was stirred under argon at room temperature. When the reaction was complete, the solvent was removed under reduced pressure, the residue was ground with 8 ml of diethyl ether, and the precipitate was filtered off and dried under reduced pressure. The mother liquor contained only unreacted acetylene **IIa**–**IIc** (identified by TLC) and phosphine oxide **I** (identified by ^{1}H and ^{31}P NMR spectroscopy).

2-(Diphenylphosphoryl)-4-phenylbut-3-yn-2-ol (IIIa) (Table 1, run no. 3**).** Yield 0.166 g (96%), white powder, mp 140–142°C (decomp.). IR spectrum, ν, cm^{-1}: 3141 (OH), 2234 w (C≡C), 1175 (P=O). ^1H NMR spectrum, δ, ppm: 1.80 d (3H, Me, $^3J_{PH}$ = 13.2 Hz), 4.00 br.s (1H, OH), 7.21–7.40 m (5H, PhC), 7.45–7.65 m (6H, *p*-H, *m*-H in PhP), 8.00–8.20 m (4H, *o*-H in PhP). ^{13}C NMR spectrum, δ_C, ppm: 25.85 d (Me, $^2J_{PC}$ = 3.7 Hz), 69.86 d (C^2, $^1J_{PC}$ = 87.0 Hz), 89.09 d (Ph**C**≡C, $^3J_{PC}$ = 7.7 Hz), 88.90 d (PhC≡**C**, $^2J_{PC}$ = 2.2 Hz), 122.83 (C^i in PhC≡), 129.1–129.6, 130.7–132.2 (Ph). ^{31}P NMR spectrum: δ_P 34.32 ppm. Found, %: C 76.56; H 5.87; P 9.09. $C_{22}H_{19}O_2P$. Calculated, %: C 76.29; H 5.53; P 8.94.

3-(Diphenylphosphoryl)-1-phenylhex-1-yn-3-ol (IIIb) (Table 1, run no. 5**).** Yield 0.144 g (77%), white powder, mp 112–114°C (decomp.). IR spectrum, ν, cm^{-1}: 3050 (OH), 2218 w (C≡C), 1170 (P=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 t (3H, Me, $^3J_{HH}$ = 7.1 Hz), 1.7–1.9 m (4H, CH_2CH_2), 3.18 br.s (1H, OH), 7.3–8.1 m (15H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.57 s (Me), 16.34 d (Me**C**H_2, $^3J_{PC}$ = 8.4 Hz), 37.89 d (Et**C**H_2, $^2J_{PC}$ = 3.6 Hz), 72.02 d (COH, $^1J_{PC}$ = 86.3 Hz), 87.04 d (C^2, $^2J_{PC}$ = 2.0 Hz), 89.65 d (C^1, $^3J_{PC}$ = 8.0 Hz), 121.62 (C^i in PhC≡), 127.68–128.28, 131.15–132.37 (Ph). ^{31}P NMR spectrum: δ_P 33.39 ppm. Found, %: C 77.29; H 5.99; P 8.26. $C_{24}H_{23}O_2P$. Calculated, %: C 76.99; H 6.19; P 8.27.

3-(Diphenylphosphoryl)-4-methyl-1-phenylpent-1-yn-3-ol (IIIc) (Table 1, run no. 7**).** Yield 0.122 g (65%), white powder, mp 112–113°C (decomp.). IR spectrum, ν, cm^{-1}: 3081 (OH), 2215 w (C≡C), 1167 (P=O). ^1H NMR spectrum, δ, ppm: 1.08 d (3H, Me, $^2J_{HH}$ = 6.9 Hz), 1.18 d (3H, Me, $^2J_{HH}$ = 6.6 Hz), 2.19 m (1H, Me_2C**H**), 3.02 br.s (1H, OH), 7.26–8.12 m (15H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.48 d (Me, $^3J_{PC}$ = 5.8 Hz), 18.67 d (Me, $^3J_{PC}$ = 3.0 Hz), 35.33 d (Me_2**C**H, $^2J_{PC}$ = 5.0 Hz), 75.89 d (COH, $^1J_{PC}$ = 82.8 Hz), 86.89 d (C^2, $^2J_{PC}$ = 2.0 Hz), 91.16 d (C^1, $^3J_{PC}$ = 8.0 Hz), 122.10 (C^i in PhC≡), 128.39–132.87 (Ph). ^{31}P NMR spectrum: δ_P 32.74 ppm. Found, %: C 77.26; H 5.97; P 8.11. $C_{24}H_{23}O_2P$. Calculated, %: C 76.99; H 6.19; P 8.27.

Tertiary bis-phosphine oxides IVa–IVc (*general procedure***) (**Table 2, run nos. 4–6**).** Diphenylphosphine oxide (**I**), 1 mmol, was added to a suspension of 0.5 mmol of acetylenic ketone **IIa**–**IIc** and 0.2 mmol of $KOH \cdot 0.5H_2O$ (water content 15%) in 6 ml of THF. The mixture was stirred under argon at room temperature, and the precipitate was filtered off, washed with diethyl ether and water, and dried under reduced pressure over $CaCl_2$. In run no. 4 (Table 2), the solvent was removed from the mother liquor to isolate 0.062 g (36%) of phosphine oxide **IIIa**.

3,4-Bis(diphenylphosphoryl)-4-phenylbutan-2-one (IVa) (Table 2, run no. 4**).** Yield 0.101 g (37%), white powder, mp 240–242°C. IR spectrum, ν, cm^{-1}: 1709 (C=O); 1193, 1179 (P=O). ^1H NMR spectrum, δ, ppm: 1.66 s (3H, Me), 4.74–4.89 m (2H, 3-H, 4-H), 6.40–6.87 m (3H, *o*-H, *p*-H in PhC), 7.11–7.91 m (22H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 32.16 (Me), 46.25 d.d (C^4, $^1J_{PC}$ = 63.1, $^2J_{PC}$ = 2.8 Hz), 56.60 d (C^3, $^1J_{PC}$ = 53.9 Hz), 126.64–127.94, 130.31–132.68 (Ph), 203.93 d.d (C=O, $^2J_{PC}$ = 1.4, $^3J_{PC}$ = 2.5 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 23.42 d ($^3J_{PP}$ = 40.2 Hz), 32.93 d ($^3J_{PP}$ = 40.2 Hz). Found, %: C 74.16; H 5.51; P 11.51. $C_{34}H_{30}O_3P_2$. Calculated, %: C 74.44; H 5.51; P 11.29.

1,2-Bis(diphenylphosphoryl)-1-phenylhexan-3-one (IVb) (Table 2, run no. 5**).** Yield 0.236 g (82%), white powder, mp 252–254°C. IR spectrum, ν, cm^{-1}: 1707 (C=O); 1190, 1174 (P=O). ^1H NMR spectrum, δ, ppm: 0.34 t (3H, Me), 0.51 m and 0.63 m (1H each, Me**C**H_2), 1.71 m and 2.57 m (1H each, Et**C**H_2), 4.73–4.84 m (2H, 1-H, 2-H), 6.45–6.96 m (3H, *o*-H, *p*-H in PhCH), 7.0–8.0 m (22H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 12.95 (Me), 15.51 (Me**C**H_2), 48.64 (**C**H_2C=O), 46.15 d.d (C^1, $^1J_{PC}$ = 62.5, $^2J_{PC}$ = 2.4 Hz), 56.15 d (C^2, $^1J_{PC}$ = 54.5 Hz), 127.16–128.45, 130.77–133.24 (Ph), 209.35 d.d (C=O, $^2J_{PC}$ = 1.0, $^3J_{PC}$ = 1.5 Hz). ^{31}P NMR spectrum, δ_P, ppm: 23.46 d ($^3J_{PP}$ = 41.50 Hz), 32.42 d ($^3J_{PP}$ = 41.50 Hz). Found, %: C 74.67; H 6.14; P 11.01. $C_{36}H_{34}O_3P_2$. Calculated, %: C 74.99; H 5.94; P 10.74.

1,2-Bis(diphenylphosphoryl)-4-methyl-1-phenylpentan-3-one (IVc) (Table 2, run no. 6**).** Yield 0.150 g (52%), white powder, mp 226–228°C. IR spectrum, ν, cm^{-1}: 1706 (C=O); 1192, 1185 (P=O). ^1H NMR spectrum, δ, ppm: 0.28 d and 0.52 d (3H each, Me, $^3J_{HH}$ = 6.9 Hz), 2.35 m (Me_2C**H**), 4.83 d.d.d (1H, 1-H, $^3J_{HH}$ = 11.3, $^2J_{PH}$ = 5.1, $^3J_{PH}$ = 6.0 Hz), 5.00 d.d.d (1H, 2-H, $^3J_{HH}$ = 11.3, $^2J_{PH}$ = 8.6, $^3J_{PH}$ = 9.0 Hz), 6.60–6.70 m (3H, *o*-H, *p*-H in PhCH), 6.9–8.0 m (22H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.25 and 17.29 (Me), 44.02 (Me_2**C**H), 45.68 d.d (C^1, $^1J_{PC}$ = 62.5, $^2J_{PC}$ = 3.0 Hz), 54.46 d (C^2, $^1J_{PC}$ = 54.7 Hz), 127.04–128.33, 130.48–132.87 (Ph), 209.35 d.d (C=O, $^2J_{PC}$ = 1.5, $^3J_{PC}$ = 3.0 Hz). ^{31}P NMR spectrum, δ_P, ppm: 24.59 d ($^3J_{PP}$ = 41.5 Hz), 32.79 d ($^3J_{PP}$ = 41.5 Hz). Found, %: C 74.75; H 6.11; P 10.53. $C_{36}H_{34}O_3P_2$. Calculated, %: C 74.99; H 5.94; P 10.74.

Tertiary phosphine oxides VIa–VIc (*general procedure***) (**Table. 3, run nos. 3–5**).** A mixture of 0.5 mmol of bis(2-phenylethyl)phosphine oxide (**V**), 0.5 mmol of acetylenic ketone **IIa**–**IIc**, and 0.1 mmol of $KOH \cdot 0.5H_2O$ (water content 15%) in 4 ml of THF was stirred for 35 h under argon at room temperature. The suspension was passed through a thin layer of aluminum oxide, the solvent was removed under reduced pressure, the residue was ground with 5 ml of diethyl ether, and the precipitate was filtered off and dried under reduced pressure.

2-[Bis(2-phenylethyl)phosphoryl]-4-phenylbut-3-yn-2-ol (VIa) (Table 3, run no. 3**).** Yield 0.135 g (67%), white powder, mp 103–105°C (decomp.). IR spectrum, ν, cm^{-1}: 3131 (OH), 2225 w (C≡C), 1158 (P=O). ^1H NMR spectrum, δ, ppm: 1.90 d (3H, Me, $^3J_{PH}$ = 12.4 Hz), 2.1–2.6 m (4H, CH_2P), 2.9–3.2 m (4H, C**H**$_2$Ph), 5.63 br.s (1H, OH), 7.2–7.4 m (15H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 24.69 d (Me, $^2J_{PC}$ = 3.6 Hz), 26.90 d (CH_2P, $^1J_{PC}$ = 60.8 Hz), 27.65 d (CH_2P, $^1J_{PC}$ = 57.2 Hz), 28.19 d (**C**H_2Ph, $^2J_{PC}$ = 3.6 Hz), 28.26 d (**C**H_2Ph, $^2J_{PC}$ = 2.8 Hz), 67.96 d (C^2, $^1J_{PC}$ = 80.0 Hz), 87.75 d (Ph**C**≡, $^3J_{PC}$ = 7.2 Hz), 88.33 d (PhC≡**C**, $^2J_{PC}$ = 2.0 Hz), 121.97 (C^i in PhC≡), 126.46 m (C^o in CH_2Ph), 128.15–128.95 (C^m, C^p in CH_2Ph, PhC≡), 131.70 (C^o in PhC≡), 141.15–141.28 (C^i in CH_2Ph). ^{31}P NMR spectrum: δ_P 51.49 ppm. Found, %: C 77.86; H 6.89; P 7.99. $C_{26}H_{27}O_2P$. Calculated, %: C 77.59; H 6.76; P 7.70.

3-[Bis(2-phenylethyl)phosphoryl]-1-phenylhex-1-yn-3-ol (VIb) (Table 3, run no. 4**).** Yield 0.136 g (63%), white powder, mp 117–119°C (decomp.). IR spectrum, ν, cm^{-1}: 3083 (OH), 2221 w (C≡C), 1145 (P=O). ^1H NMR spectrum, δ, ppm: 1.05 t (3H, Me, $^3J_{HH}$ = 7.0 Hz), 1.87 m (2H, MeC**H**$_2$), 2.1–2.6 m (6H, CH_2P, EtC**H**$_2$), 2.9–3.2 m (4H, C**H**$_2$Ph), 4.32 br.s (1H, OH), 7.2–7.4 m (15H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 14.30 s (Me), 16.91 d (Me**C**H_2, $^3J_{PC}$ = 7.9 Hz), 27.11 d (PCH_2, $^1J_{PC}$ = 60.0 Hz), 27.60 d (PCH_2, $^1J_{PC}$ = 58.0 Hz), 28.23 s (Ph**C**H_2), 38.33 d (Et**C**H_2, $^2J_{PC}$ = 2.4 Hz), 71.40 d (C^3, $^1J_{PC}$ = 79.5 Hz), 87.15 d (C^2, $^2J_{PC}$ = 1.9 Hz), 88.72 d (C^1, $^3J_{PC}$ = 7.6 Hz), 122.01 (C^i in PhC≡), 126.39 m (C^o in CH_2Ph), 128.14–128.88 (C^m, C^p in CH_2Ph, PhC≡), 131.73 (C^o in PhC≡), 141.21–141.65 (C^i in CH_2Ph). ^{31}P NMR spectrum: δ_P 51.45 ppm. Found, %: C 78.38; H 7.49; P 7.31. $C_{28}H_{31}O_2P$. Calculated, %: C 78.12; H 7.26; P 7.19.

3-[Bis(2-phenylethyl)phosphoryl]-4-methyl-1-phenylpent-1-yn-3-ol (VIc) (Table 3, run no. 5). Yield 0.041 g (19%), white powder, mp 117–118°C (decomp.). IR spectrum, ν, cm^{-1}: 3132 (OH), 2225 w (C≡C), 1144 (P=O). ^1H NMR spectrum, δ, ppm: 1.23 d (3H, Me, $^3J_{HH}$ = 6.3 Hz), 1.25 d (3H, Me, $^3J_{HH}$ = 6.0 Hz), 2.11–2.40 m (4H, PCH_2), 2.88–3.20 m (5H, C**H**$_2$Ph, OH), 7.2–7.4 m (15H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.04 d (Me, $^3J_{PC}$ = 4.8 Hz), 18.37 d (Me, $^3J_{PC}$ = 1.8 Hz), 27.79 s (Ph**C**H_2), 28.01 d (PCH_2, $^1J_{PC}$ = 61.9 Hz), 34.74 d (CH, $^2J_{PC}$ = 2.6 Hz), 74.38 d (C^3, $^1J_{PC}$ = 77.0 Hz), 85.71 d (C^2, $^2J_{PC}$ = 1.0 Hz), 89.27 d (C^1, $^3J_{PC}$ = 7.4 Hz), 121.47 (C^i in PhC≡), 125.92, 126.03 (C^o in CH_2Ph), 127.66–128.54 (C^m, C^p in CH_2Ph, PhC≡), 131.32 (C^o in PhC≡), 140.80, 141.11 (C^i in CH_2Ph). ^{31}P NMR spectrum ($CDCl_3$): δ_P 52.91 ppm. Found, %: C 78.30; H 7.32; P 7.61. $C_{28}H_{31}O_2P$. Calculated, %: C 78.12; H 7.26; P 7.19.

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