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Chemoselective Noncatalytic Addition of Secondary Phosphine Chalcogenides to Citral

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Abstract — Addition of secondary phosphine oxides, phosphine sulfides and phosphine selenides to 3,7-dimethyl-2,6-octadienal (citral) (48–50°C, THF, argon) proceeds exclusively to the aldehyde group giving rise to new polyfunctional tertiary phosphine chalcogenides with diene and hydroxyl moieties in high preparative yield (up to 80%).
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Organic phosphine chalcogenides are widely known as effective ligands for preparation of metal complex catalysts, materials for microelectronics, coherent and nonlinear optics, antipyrenes, extractive agents for rare earth and transuranium elements, flotoreagents, emulgators, biologically active compounds for medicine and agriculture [1–14]. Recently, tertiary phosphine chalcogenides were effectively applied to preparation of unique semiconducting nanomaterials [15]. In the last years there is a growing interest to water soluble and hydrophilic organophosphorus ligands (for example, possessing hydroxyl functions) used for design of metal complex catalysts for phase transfer reactions [16]. One of practical approaches to the synthesis of these compounds is the reaction of nucleophilic addition of secondary phosphine chalcogenides to aldehydes, which is actively worked out on the example of hydrophosphorylation of aromatic and heteroaromatic aldehydes with secondary phosphine oxides [17–25] and, to a lesser extent, with secondary phosphine sulfides [25–31]. As to secondary phosphine selenides, to the best of our knowledge, there are no data in the literature on hydroselenophosphorylation of aldehydes.

In the present work, with the aim of investigation of regularities of the reaction of aldehydes with secondary phosphine chalcogenides and expansion of its synthetic possibilities, we for the first time have performed the reaction of readily available diphenylphosphine oxide (**Ia**), bis(2-phenylethyl)phosphine oxide (**Ib**) [32], bis(2-phenylethyl)phosphine sulfide (**Ic**) [33], bis(2-phenyl-ethyl)phosphine selenide (**Id**) [34] with (*Z/E*)-3,7-di-methyl-2,6-octadienal (**II**) (citral) polyunsaturated natural aldehyde (the major component of lemon, eucalyptus and verbena fragrant oils [35–38]), synthesized by us on the basis of acetylene by modified technology [39, 40].

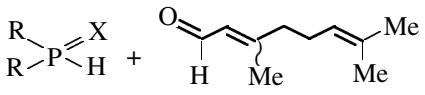
The course of the reaction could not be unequivocally predicted: the addition could occur either to the double bonds of the unsaturated aldehyde **II** or to the carbonyl group, so, the question which of these electrophilic centers would be more complementary to secondary phosphine chalcogenides remained open.

It turned out that hydrochalcogenophosphorylation of octadienal **II** with secondary phosphine chalcogenides **Ia**–**Id** proceeds chemoselectively to the carbonyl group with the formation of the corresponding (*Z/E*)-1-(diorganylchalcogenophosphoryl)-3,7-dimethyl-2,6-octadien-1-ols (**IIIa**–**IIId**).

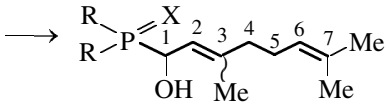
The process is realized under mild noncatalytic conditions (48–50°C, 11–29 h, inert atmosphere, THF) with the use of equimolar amounts of the reagents, the yield of adducts **III** is 68–80%.

The starting citral was the mixture of isomers *Z*:*E* in the ratio of 63:37 (from the ^{1}H NMR spectroscopy). The percentage of the *Z*-isomer in the obtained adducts **IIIa**–**IIId** is retained at the same level (63–73%).

In the ^{1}H and ^{13}C NMR spectra of the *Z/E*-isomers of phosphine chalcogenides **IIIa**–**IIId** the most



Ia–Ir **II**



IIIa–IIId

X = O, R = Ph (**a**), $Ph(CH_2)_2$ (**b**); X = S, R = $Ph(CH_2)_2$ (**c**); X = Se, R = $Ph(CH_2)_2$ (**d**).

characteristic signals are those of the CH group of fragment HOCHP=X, which are displayed as a doublet of doublets at 4–5 ppm with geminal spin–spin coupling constant $^{31}P–^{1}H$ equal to 2–3 Hz and a large vicinal constant $^{3}J_{HH}$ ~9–10 Hz (^{1}H). In the ^{13}C NMR spectra they are represented as a doublet at 67–68 ppm with the coupling constant $^{1}J_{PC}$ ~48–77 Hz. The nonequivalence of the signals of the two phenylethyl groups in the ^{1}H and ^{13}C NMR spectra of phosphine chalcogenides **IIIa–IIId** is due to prochirality of these groups at the phosphorus atom. Small value of $^{2}J_{HP}$ in the proton spectra could be indicative of a substantial contribution of the rotamer with the dihedral angle X=P–C–H close to 180°C [41].

In the IR spectrum of tertiary phosphine oxide **IIIa** the stretching vibrations of the C=C bonds are represented by a band with absorption maximum at 1653 cm^{-1} and the shoulder at 1660 cm^{-1}, and those of phosphinechalcogenides **IIIb–IIId** by a band with absorption maximum at 1665–1670 cm^{-1} and the shoulder at 1653–1657 cm^{-1}. The stretching vibrations of the P=O bond in the spectra of tertiary phosphine oxides **IIIa** and **IIIb** are observed at 1164 and 1142 cm^{-1}, respectively. At the same time, the stretching vibrations of the P=S bond in the IR spectra of phosphine sulfide **IIIc** and P=Se bond in the IR spectra of phosphine selenide **IIId** are substantially shifted to low frequency region and are represented by the corresponding absorption bands at 590 with the shoulder at 579 cm^{-1} and 470 with the shoulder at 491 cm^{-1}. Stretching vibrations of the hydroxyl group (ν_{OH}) in compounds **IIIa–IIId** are observed as a wide band at 3100–3400 cm^{-1} (KBr and Vaseline oil) and the corresponding deformation vibrations (δ_{COH}) at 1092–1099 cm^{-1}.

In the IR spectra of solutions (CCl_4, *C* 0.1 M) of α-hydroxyphosphine oxides **IIIa**, **IIIb** an intense ν_{OH} band is observed at 3183–3200 cm^{-1} with the shoulder at 3376 cm^{-1}, as well as a weak band at 3600 cm^{-1}. Upon subsequent dilution (*C* ~0.002 M) the first two bands disappear whereas the band at 3600 cm^{-1} retains its position. These data suggest that the bands in the region 3183–3376 cm^{-1} refer to stretching vibrations of OH groups involved in intermolecular hydrogen bonds, whereas the stretching vibrations of the free OH group are characterized by the high frequency band at 3600 cm^{-1}. In the spectra of diluted solutions of α-hydroxyphosphine oxides **IIIa**, **IIIb** (*C* ~0.002 M, *d* 10 cm) no band of stretching vibrations of OH group involved in intramolecular hydrogen bonding is found. Apparently, a bulky nonadienyl radical causes spatial blockage of the hydroxyl group.

Therefore, chemoselective reaction of citral with secondary phosphine chalcogenides is an expedient atom–economic method for synthesis of tertiary polyfunctional phosphine chalcogenides new prospective polydentate chiral ligands for enantioselective processes, highly reactive synthons for organic synthesis and preparation of biologically active compounds.

EXPERIMENTAL

Commercial diphenylphosphine oxide (Alfa Aesar, Germany) was used. Bis(2-phenylethyl)phosphine oxide was synthesized according to [33], bis(2-phenyl-ethyl)phosphine sulfide according to [34], bis(2-phenylethyl)phosphine selenide according to [35], citral according to [40].

^{1}H, ^{13}C and ^{31}P NMR spectra were registered on a Bruker DPX-400 spectrometer (400.13, 101.61 and 161.98 MHz, respectively) in $CDCl_3$, internal standard HMDS, external standard 85% H_3PO_4. IR spectra were recorded on a Bruker IFS 25 spectrometer in pellets of KBr, vaseline oil and CCl_4 solution. The reactions were followed by the use of ^{31}P NMR spectroscopy by decrease of intensity of the signals of starting diorganylphosphine chalcogenides **Ia–Id** at 2–21 ppm and by appearance and increase of the signals of tertiary α-hydroxyphosphine chalcogenides **IIIa–IIId** at 29–59 ppm.

(*Z*/*E*)-3,7-Dimethyl-2,6-octadienal (I) (the ratio of *Z*:*E*-isomers = 63:37). ^{1}H NMR ($CDCl_3$), δ_H, ppm for the ***Z*-isomer**: 1.67 s, 1.60 s [6H, $C^7–(CH_3)_2$], 2.15 d (3H, $C^3–CH_3$, $^{2}J_{HH}$ 1.26 Hz), 2.21 m (4H, $C^4–H_2$, $C^5–H_2$), 5.06 t. m (1H, $=C^6–H$, $^{3}J_{HH}$ 6.90, $^{4}J_{HH}$ 1.43 Hz), 5.86 d. m (1H, $=C^2–H$, $^{3}J_{HH}$ 8.11, $^{4}J_{HH}$ 1.32 Hz), 9.98 d ($C^1–H$, $^{3}J_{HH}$ 8.11 Hz); for the ***E*-isomer:** 1.67 s, 1.58 s [6H, $C^7–(CH_3)_2$], 1.97 d (3H, $C^3–CH_3$, $^{2}J_{HH}$ 1.32 Hz), 2.58 t (2H, $C^4–H_2$, $^{3}J_{HH}$ 7.45 Hz), 2.21 m (2H, $C^5–H_2$), 5.09 t.m (1H, $=C^6–H$,

$^3J_{HH}$ 7.34 Hz, $^4J_{HH}$ 1.43 Hz), 5.86 d.m (1H, =C^2–H, $^3J_{HH}$ 8.11, $^4J_{HH}$ 1.32 Hz), 9.88 d (C^1–H, $^3J_{HH}$ 8.11 Hz).

1-(Diorganylchalcogenophosphoryl)-3,7-dimethyl-2,6-octadien-1-ol (IIIa–IIId) *(general procedure).* Mixture of 1.2 mmol of diorganylphosphine chalcogenide **Ia–d** and 1.2 mmol of aldehyde **II** in 5 ml of THF was bubbled with argon and stirred at 48–50°C: for diorganylphosphine oxides **Ia**, **Ib** for 11 and 21 h, respectively, for phosphine sulfide **Ic** 29 h, for phosphine selenide **Id** 11 h. the solvent was removed in vacuum, the residue (for **IIIa–IIIc**) washed with small portions of hexane (0.3 ml × 4), crystallized from hexane; product **IIId** (syrupous substance) was purified by reprecipitation from chloroform into petroleum ether. Products **IIIa–IIId** were obtained as mixtures of the *Z/E*-isomers.

(*Z/E*)-1-(Diphenylphosphoryl)-3,7-dimethyl-2,6-octadien-1-ol (IIIa) (the ratio of **Z : E**-isomers = 63 : 37). Yield 97%, mp 69–71°C. Found, %: C 74.22; H 7.61; P 8.48. $C_{22}H_{27}O_2P$. Calculated, %: C 74.55; H 7.68; P 8.74. ^{1}H NMR ($CDCl_3$), δ_H, ppm. for ***Z*-isomer:** 1.41 s (3H, C^3–CH_3), 1.52 s, 1.61 s [6H, C^7–$(CH_3)_2$], 1.82–1.92 m(4H, C^4–H_2, C^5–H_2), 4.96 m (1H, C^2–H), 7.42–7.88 (10H, Ph); for ***E*-isomer:** 1.51 s, 1.62 s [6H, C^7–$(CH_3)_2$], 1.67 s (3H, C^3–CH_3), 1.82–1.92 m (4H, C^4–H_2, C^5–H_2), 4.96 m (C^6–H), 5.07 d (1H, C^1–H, $^3J_{HH}$ 9.9 Hz), 5.28 m (1H, C^2–H), 7.42–7.88 (2H, H_m). ^{13}C NMR ($CDCl_3$), δ_C, ppm, for ***Z*-isomer:** 17.07 (C^3–CH_3), 23.64 (C^5), 26.28 [C^7–$(CH_3)_2$], 39.86 (C^4), 69.10 d (C^1–H, $^1J_{PC}$ 60.6 Hz), 119.19 (C^2), 123.72 (C^6), 128.40 d (C_o, $^2J_{PC}$ 13.0 Hz), 128.50 d (C_o, $^2J_{PC}$ 13.0 Hz), 131.80 d (C_m, $^3J_{PC}$ 11.0 Hz), 132.00 d (C_m, $^3J_{PC}$ 11.0 Hz), 132.13 (C_p), 132.47 (C^7), 143.69 (C_i, Ph), 143.69 (C^3); for ***E*-isomer:** 17.76 d (C^3–CH_3, $^4J_{PC}$ 4.98 Hz), 23.64 (C^5), 25.71 [C^7–$(CH_3)_2$], 32.57 (C^4), 68.25 d (C^1–H, $^1J_{PC}$ 63.3 Hz), 119.52 (C^2), 123.72 (C^6), 128.40 d (C_o, $^2J_{PC}$ 13.0 Hz), 128.50 d (C_o, $^2J_{PC}$ 13.0 Hz), 131.80 d (C_m, $^3J_{PC}$ 11.0 Hz), 132.00 d (C_m, $^3J_{PC}$ 11.0 Hz), 132.13 (C_p), 132.47 (C^7), 143.69 (C_i, Ph), 143.69 (C^3). ^{31}P NMR ($CDCl_3$), δ_P, ppm for ***Z*-isomer:** 29.65; for ***E*-isomer:** 28.68.

IR (KBr, cm^{-1}): 3394, 3186 ν(OH), 3076, 3055, 3009 ν(=CH of vinyl and phenyl groups), 2968, 2912, 2853 ν(CH), 1660, 1653 ν(C=C of vinyl group), 1591, 1484, 1450 ν(C=C of phenyl rings), 1164 ν(P=O), 1099 δ(COH).

(*Z/E*)-1-(Diphenylethylphosphoryl)-3,7-dimethyl-2,6-octadien-1-ol (IIIb) (the ratio of *Z : E*-isomers = 71 : 29). Yield 76%, mp 69–71°C. Found, %: C 76.28; H 8.56; P 7.30. $C_{26}H_{35}O_2P$. Calculated, %: C 76.07; H 8.59; P 7.54. ^{1}H NMR ($CDCl_3$), δ_H, ppm for ***Z*-isomer:** 1.52 s, 1.58 s [6H, C^7–$(CH_3)_2$], 1.72 d (3H, C^3–CH_3, $^4J_{HH}$ 1.28 Hz), 1.82 m, 2.23 m (4H, C^4–H_2, C^5–H_2), 2.09 m (4H, CH_2P), 2.93 m (4H, $PhCH_2$), 4.73 d (1H, C^1–H, $^3J_{HH}$ 9.20 Hz), 5.00 m (1H, C^6–H), 5.34 d.d (1H, C^2–H, $^3J_{HH}$ 9.2, $^3J_{PH}$ 4.13 Hz), 7.02 m, 7.42 m (10H, Ph); for ***E*-isomer:** 1.57 s, 1.65 s [6H, C^7–$(CH_3)_2$], 1.80 d (3H, C^3–CH_3, $^4J_{HH}$ 2.05 Hz), 1.82 m, 2.23 m (4H, C^4–H_2, C^5–H_2), 2.09 m (4H, CH_2P), 3.00 m (4H, $PhCH_2$), 4.65 d (1H, C^1–H, $^3J_{HH}$ 9.60 Hz), 5.07 br.t (1H, C^6–H, $^3J_{HH}$ 6.30 Hz), 5.40 d.d (1H, C^2–H, $^3J_{HH}$ 9.6, $^3J_{PH}$ 6.00 Hz), 7.02 m, 7.42 m (10H, Ph). ^{13}C NMR ($CDCl_3$), δ_C, ppm for ***Z*-isomer:** 14.47 (C^3–CH_3), 25.75 (C^5), 26.26 [C^7–$(CH_3)_2$], 27.46 d (CH_2P, $^1J_{PC}$ 36.8 Hz), 27.86 ($PhCH_2$), 39.95 (C^4), 67.67 d (C^1–H, $^1J_{PC}$ 77.20 Hz), 119.65 (C^2), 123.56 (C^6), 126.50 (C_p), 128.15 d (C_o, $^4J_{PC}$ 4.3 Hz), 128.72 (C_m), 132.21 (C^7), 141.36 d (C_i, $^3J_{PC}$ 13.3 Hz), 143.23 (C^3); for ***E*-isomer:** 17.75 (C^3–CH_3), 25.75 (C^5), 26.53 [C^7–$(CH_3)_2$], 27.46 d (CH_2P, $^1J_{PC}$ 36.80 Hz), 27.86 ($PhCH_2$), 32.81 (C^4), 67.70 d (C^1–H, $^1J_{PC}$ 57.76 Hz), 119.95 (C^2), 123.56 (C^6), 126.50 (C_p), 128.15 (C_o), 128.72 (C_m), 132.21 (C^7), 141.36 d (C_i, $^3J_{PC}$ 13.3 Hz), 143.23 (C^3). ^{31}P NMR ($CDCl_3$), δ_P, ppm for ***Z*-isomer:** 50.81; for ***E*-isomer:** 49.82. IR (KBr, cm^{-1}): 3406, 3148 ν(OH), 3085, 3061, 3029, 3028 ν(=CH of vinyl and phenyl groups), 2958, 2924, 2864 ν(CH), 1665, 1654 ν(C=C of vinyl group), 1603, 1584, 1496, 1453 ν(C=C of phenyl rings), 1142 ν(P=O), 1092 δ(COH).

(*Z/E*)-1-(Diphenylethylthiophosphoryl)-3,7-dimethyl-2,6-octadien-1-ol (IIIc) (the ratio of *Z : E*-isomers = 73 : 27). Yield 68%, mp 75–76°C. Found, %: C 73.62; H 8.20; P 7.14; S 7.44. $C_{26}H_{35}OPS$. Calculated, %: C 73.20; H 8.27; P 7.26; S 7.52. ^{1}H NMR ($CDCl_3$), δ_H, ppm for ***Z*-isomer:** 1.51 s, 1.56 s [6H, C^7–$(CH_3)_2$], 1.72 d. d (3H, C^3–CH_3, $^4J_{HH}$ 1.28, $^5J_{PH}$ 3.07 Hz), 2.12 m (4H, C^4–H_2, C^5–H_2), 1.90–2.20 m (4H, CH_2P), 2.93 m (4H, $PhCH_2$), 4.56 d (1H, C^1–H, $^3J_{HH}$ 9.98 Hz), 4.99 br. t (1H, C^6–H, $^3J_{HH}$ 5.90 Hz), 5.28 d.d (1H, C^2–H, $^3J_{HH}$ 9.98, $^3J_{PH}$ 5.38 Hz), 7.11–7.32 m (10H, Ph); for ***E*-isomer:** 1.65 s, 1.67 s [6H, C^7–$(CH_3)_2$], 1.81 d.d (3H, C^3–CH_3, $^4J_{HH}$ 1.28, $^5J_{PH}$ 3.33 Hz), 2.12 m (4H, C^4–H_2, C^5–H_2),

1.90–2.20 m (4H, CH_2P), 2.93 m (4H, $PhCH_2$), 4.55 d (1H, C^1–H, $^3J_{HH}$ 9.98 Hz), 5.06 br.t (1H, C^6–H, $^3J_{HH}$ 5.90 Hz), 5.32 d. d (1H, C^2–H, $^3J_{HH}$ 9.98, $^3J_{PH}$ 6.0 Hz), 7.11–7.32 m (10H, Ph). ^{13}C NMR ($CDCI_3$), δ_C, ppm for ***Z*-isomer:** 17.60 (C^3–CH_3), 25.78 [C^7–$(CH_3)_2$], 28.59 ($PhCH_2$), 28.81 (C^5), 29.95 d (CH_2P, $^1J_{PC}$ 45.8 Hz), 40.02 (C^4), 67.76 d (C^1–H, $^1J_{PC}$ 56.5 Hz), 119.20 (C^2), 123.47 (C^6), 126.63 (C_p), 128.31 (C_o), 128.80 (C_m), 132.39 (C^7), 140.94 d (C_i, $^3J_{PC}$ 15.90 Hz), 144.07 (C3); for ***E*-isomer:** 17.76 (C^3–CH_3), 25.73 [C^7–$(CH_3)_2$], 28.59 ($PhCH_2$), 28.86 (C^5), 29.54 d (CH_2P, $^1J_{PC}$ 48.5 Hz), 32.99 (C^4), 67.32 d (C^1–H, $^1J_{PC}$ 57.0 Hz), 119.55 (C^2), 123.30 (C^6), 126.68 (C_p), 128.27 (C_o), 128.80 (C_m), 132.39 (C^7), 140.94 d (C_i, $^3J_{PC}$ 15.9 Hz), 144.00 (C^3). ^{31}P NMR ($CDCI_3$), δ_P, ppm for ***Z*-isomer:** 59.17; for ***E*-isomer:** 57.88.

IR (KBr, cm^{-1}): 3417 ν(OH), 3103, 3083, 3061, 3025 ν(=CH of vinyl and phenyl groups), 2959, 2931, 2908, 2449, ν(CH), 1661, 1653 ν(C=C of vinyl group), 1600, 1584, 1495, 1452 ν(C=C of phenyl rings), 1093 ν(COH), 590, 579 δ(P=S).

(*Z*/*E*)-1-(Diphenylethylselenophosphoryl)-3,7-dimethyl-2,6-octadien-1-ol (IIId) (the ratio of *Z*:*E*-isomers = 73:27). Yield 80%, syrupous substance. Found, %: C 66.28; H 7.46; P 6.48; Se 16.37. $C_{26}H_{35}OPSe$. Calculated, %: C 65.95; H 7.45; P 6.54; Se 16.68. ^1H NMR ($CDCl_3$), δ_H, ppm for ***Z*-isomer:** 1.50 s, 1.55 s [6H, C^7–$(CH_3)_2$], 1.72 d. d (3H, C^3–CH_3, $^4J_{HH}$ 1.3, $^5J_{PH}$ 3.1 Hz), 2.12 m (4H, C^4–H, C^5–H), 2.18 m (4H, CH_2P), 2.93 m (4H, $PhCH_2$), 4.57 d.d (1H, C^1–H, $^3J_{HH}$ 10.03, $^2J_{PC}$H 2.35 Hz), 4.98 br.t (1H, C^6–H, $^3J_{HH}$ 6.8 Hz), 5.28 d. d. q (1H, C^2–H, $^3J_{HH}$ 10.03, $^3J_{PH}$ 5.17, $^4J_{HH}$ 1.34 Hz), 7.1–7.28 m (10H, Ph); for ***E*-isomer:** 1.64 s, 1.66 s [6H, C^7–$(CH_3)_2$], 1.81 d.d (3H, C^3–CH_3, $^4J_{HH}$ 1.38, $^5J_{PH}$ 3.48 Hz), 2.12 m (2H, C^4–H, C^5–H), 2.18 m (4H, CH_2P), 2.93 m (4H, $PhCH_2$), 4.56 d.d (1H, C^1–H, $^3J_{HH}$ 10.09, $^2J_{PC}$ 2.00 Hz), 5.05 br.t (1H, C^6–H, $^3J_{HH}$ 6.48 Hz), 5.31 d.d.q (1H, C^2–H, $^3J_{HH}$ 10.09, $^3J_{PH}$ 6.70, $^4J_{HH}$ 1.38 Hz), 7.15–7.28 m (10H, Ph). ^{13}C NMR ($CDCl_3$), δ_C, ppm for ***Z*-isomer:** 17.99 (C^3–CH_3), 26.08 [C^7–$(CH_3)_2$], 26.40 (C^5), 28.73 d (CH_2P, $^1J_{PC}$ 37.0 Hz), 29.88 d ($PhCH_2$, $^2J_{PC}$ 18.0 Hz), 40.29 (C^4), 67.25 d (C^1–H, $^1J_{PC}$ 48.0 Hz), 119.26 (C^2), 123.72 (C^6), 126.96 (C_p), 128.62 (C_o), 129.08 (C_m), 132.69 (C^7), 142.00 (C_i), 145.00 (C^3); for ***E*-isomer:** 18.05 (C^3–CH_3), 26.02 [C^7–$(CH_3)_2$], 26.81 (C^5), 28.88 d (CH_2P, $^1J_{PC}$ 37.0 Hz), 29.41 d ($PhCH_2$, $^2J_{PC}$ 18.0 Hz), 39.00 (C^4), 66.80 d (C^1–H, $^1J_{PC}$ 48.0 Hz), 119.70 (C^2), 123.51 (C^6), 126.69 (C_p), 128.76 (C_o), 128.96 (C_m), 133.0 (C^7), 140.16 (C_i), 145.3 (C^3). ^{31}P NMR ($CDCl_3$), δ_P, ppm for ***Z*-isomer:** 50.54; for ***E*-isomer:** 49.39.

IR (KBr, cm^{-1}): 3360 ν(OH), 3106, 3084, 3062, 3027 ν(=CH of vinyl and phenyl groups), 2967, 2925, 2856 ν(CH), 1670, 1657 ν(C=C of vinyl group), 1602, 1584, 1496, 1453 ν(C=C of phenyl rings), 1093 δ(COH), 491, 470 ν(P=Se).

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REFERENCES

1. Flett, D.S., *Organomet. Chem.,* 2005, vol. 690, p. 2426.
2. Szczepura, L.F., Ooro, B.A., and Wilson, S.R., *J. Chem. Soc., Dalton Trans.,* 2002, vol. 16, p. 3112.
3. Doux, M., Moores, A., Mezailles, N., Ricard, L., Jean, Y., and Le Floch, P., *J. Organomet. Chem.,* 2005, vol. 690, p. 2407.
4. Belletti, D., Graiff, C., Masser, C., Pattacini, R., Predieri, G., and Tiripicchio, A., *Inorg. Chim. Acta.,* 2003, vol. 356, no. 3, p. 187.
5. Adam, R.D., Kwon, O.S., and Sanyal, S., *Organomet. Chem.,* 2003, vol. 681, p. 258.
6. Malik, S., Duddeck, H., Omelanczuk, J., and Choudhary, M., *Chirality,* 2002, vol. 14, p. 407.
7. Bushuk, B.A., Bushuk, S.B., Cherepennikova, N.F., Douglas, W.E., Fukin, G.K., Grigoriev, I.S., Klapshina, L.G., van der Lee, A., and Semenov, V.V., *Mendeleev Cmmun.,* 2004, vol. 14, no. 3, p. 109.
8. Gusarova, N.K., Trofimov, B.A., Malysheva, S.F., Sukhov, B.G., Kuimov, V.A., Belogorlova, N.A., Smirnov, V.I., and Kurmankulov, N.B., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 4, p. 635.
9. Sukhov, B.G., Malysheva, S.F., Martynovich, E.F., Illarionov, A.I., Tirskii, V.V., Starchenko, A.A., Dubrovina, M.A., Belogorlova, N.A., Gusarova, N.K., and Trofimov, B.A., *Dokl. Akad. Nauk,* 2004, vol. 394, no. 2, p. 34.
10. Dafeng, X. and Takashi K., *Electroanalysis,* 2001, vol. 13, no. 10, p. 868.
11. Archer, C.M., Dilworth, J.R., Griffiths, D.V., Hughes, J.M., Kelly, J.D., and Morton, S., in *Technetium*

in Chemistry and Nuclear Medicine, Nicolini, M., Bandoli, G., and Mazzi, U., Eds.; SGEditoriali: Padova, 1995, p. 173.

12. Yudelevich, V.I., Komarov, E.V., and Ionin, B.I., *Khim. Pharm. Zh.,* 1985, vol. 19, no. 6, p. 668.
13. Haynes, R.K., Lam, W.W.-L., and Yeung, L.-L., *Tetrahedron Lett.,* 1996, vol. 37, no. 27, p. 4729.
14. Erastov, O.A. and Nikonov, G.N., *Funktsionalnozameshchennye fosfiny i ikh proizvodnye* (Functionally Substituted and Derivatives), Moscow: Nauka, 1986.
15. Gubin, S.P., Kataeva, N.A., and Khomutov, G.B., *Russ. Chem. Bull.,* 2005, vol. 54, no. 4, p. 827; Pavithran, R., Reddy, M.L.P., Junior, S.A., Freire, R.O., Rocha, G.B., and Lima, P.P., *Eur. J. Inorg. Chem.,* 2005, p. 4129; Mann, T. and Riegler, J., *Chem. Eur. J.,* 2002, vol. 8, no. 20, p. 4791.
16. O'Brien, P. and Warren, S., *Tetrahedron Lett.,* 1995, vol. 36, no. 15, p. 2681.
17. Ivanova, N.I., Gusarova, N.K., Konovalova, N.A., Sinegovskaya, L.M., Samoilov, V.G., Markosyan, S.M., Avseenko, N.D., Sukhov, B.G., and Trofimov, B.A., *Russ. J. Gen. Chem.,* 2006, vol. 76, no. 1, p. 98.
18. Baikalova, L.V., Zyryanova, I.A., Chipanina, N.N., Sinegovskaya, L.M., Ivanova, N.I, Mamaseva, T.V., Gusarova, N.K., Afonin, A.V., and Trofimov, B.A., *Russ. J. Gen. Chem.,* 2005, vol. 75, no. 2, p. 200.
19. Ivanova, N.I., Gusarova, N.K., Nikitina, E.A., Albanov, A.I., Sinegovskaya, L.M., Nikitin, M.V., Konovalova, N.A., and Trofimov, B.A., *Phosph. Sulfur, Silicon, Relat. Elem.,* 2004, vol. 179, no. 1, p. 7.
20. Ivanova, N.I., Gusarova, N.K., Nikitina, E.A., Medvedeva, S.A., Alpert, M.L., and Trofimov, B.A., *Chem. Heterocycl. Comp.,* 2004, vol. 40, no. 4, p. 426.
21. Chipanina, N.N., Baikalova, L.V., Sinegovskaya, L.M., Kanitskaya, L.V., Fedorov, S.V., Zyryanova, I.A., Ivanova, N.I., Reutskaya, A.M., Tiunov, M.P., Gusarova, N.K., and Trofimov, B.A., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 4, p. 540.
22. Ivanova, N.I., Reutskaya, A.M., Gusarova, N.K., Medvedeva, S.A., Afonin, A.V., Ushakov, I.A., Tatarinova, A.A., and Trofimov B.A., *Russ. J. Gen. Chem.,* 2003, vol. 73, no. 9, p. 1354.
23. Gusarova, N.K., Reutskaya, A.M., Ivanova, N.I., Medvedeva, A.S., Demina, M.M., Novopashin, P.S., Afonin, A.V., Albanov, A.I., and Trofimov, B.A., *J. Organomet. Chem.,* 2002, vol. 659, p. 172.
24. Gusarova, N.K., Arbuzova, S.N., Reutskaya, A.μ., Ivanova, N.I., Baikalova, L.V., Sinegovskaya, L.M., Chipanina, N.N., Afonin, A.V., and Zyryanova, I.A., *Chem. Heterocycl. Comp.,* 2002, no. 1, p. 65.
25. Well, M. and Schmutzler, R., *Phosph. Sulfur, Silicon, Relat. Elem.,* 1992, vol. 72, p. 171.
26. Emoto, T., Gomi, H., Yoshifuji, M., Okazaki, R., and Inamoto, N., *Bull. Chem. Soc. Jpn.,* 1974, vol. 47, no. 10, p. 2449.
27. Peters, G., *J. Org. Chem.,* 1962, vol. 27, p. 2198.
28. Ivanova, N.I., Baikalova, L.V., Konovalova, N.A., Zyryanova, I.A., Albanov, A.I., Sinegovskaya, L.M., Kukhareva, V.A., Tatarinova, A.A., Avseenko, N.D., Sukhov, B.G., Gusarova, N.K., and Trofimov, B.A., *Chem. Heterocycl. Comp.,* 2005, vol. 41, no. 3, p. 317.
29. Trofimov, B.A., Gusarova, N.K., Ivanova, N.I., Konovalova, N.A., Bogdanova, M.V., Albanov, A.I., Avseenko, N.D., and Sukhov, B.G., *Russ. J. Gen. Chem.,* 2004, vol. 74, no. 10, p. 1625.
30. Gusarova, N.K., Ivanova, N.I., Bogdanova, M.V., Konovalova, N.A., Avseenko, N.D., and Sukhov B.G., Abstract of Papers, *XVII Mezhdunarodnaya nauchno-tekhnicheskaya konferentsiya "Khimicheskie reaktivy, reagenty i protsessy malotonnazhnoi khimii"* (XVII International Conf. "Chemical Reactives, Reagents, and Process of Low-Batch Chemistry") Ufa, 2004, p. 45.
31. Gusarova, N.K., Ivanova, N.I., Konovalova, N.A., Avseenko, N.D., Sukhov, B.G., Larina, L.I., and Trofimov, B.A., Abstract of Papers, *The 7th IUPAC International Conference on the Heteroatom Chemistry,* Shanghai, 2004, p. 115.
32. Gusarova, N.K., Malysheva, S.F., Arbuzova, S.N., and Trofimov, B.A., *Russ. Chem. Bull.,* 1998, vol. 47, p. 1645; Trofimov, B.A., Arbuzova, S.N., and Gusarova, N.K., *Russ. Chem. Rev.,* 1999, vol. 68, p. 215.
33. Gusarova, N.K., Bogdanova, M.V., Ivanova, N.I., Chernysheva, N.A., Sukhov, B.G., Sinegovskaya, L.M., Kazheva, O.N., Aleksandrov, G.G., D'yachenko, O.A., and Trofimov, B.A., *Synthesis,* 2005, no. 18, p. 3103.
34. Sukhov, B.G., Gusarova, N.K., Ivanova, N.I., Bogdanova, M.V., Kazheva, O.N., Aleksandrov, G.G., D'yachenko, O.A., Sinegovskaya, L.M., Malysheva, S.F., and Trofimov, B.A., *J. Struct. Chem.,* 2005, vol. 46, no. 6, p. 1066.
35. Kikonyogo, A., Abriola, D.P., Dryjanski, M., and Pietruszko, R., *Eur. J. Biochem.,* 1999, vol. 262, p. 704.
36. Wilson, N.D., Ivanova, M.S., Watt, R.A., and Moffat, A.C., *J. Pharmacy and Pharmacol.,* 2002, vol. 54, no. 9, p. 1257.
37. Do Vale, T.G., Furtado, E.C., Santos, J.G., and Viana, G.S., *Phytomedicine,* 2002, vol. 9, no. 8, p. 709.
38. *Comprehensive Organic Chemistry,* Barton, D. and Ollis, W.D., New York: Pergamon, 1979, vol. 2.

39. Trofimov, B.A., Vasil'tsov, A.M., Mikhaleva, A.I., Sobenina, L.N., and Stankevich, V.K., *Sposob polucheniya tsitraliya* (A Method for the Synthesis of Cytral), RF Patent no. 2091364, *Bull. Izobret.,* 1997, no. 27.
40. Mikhaleva, A.I., Vasil'tsov, A.M., Sobenina, L.N., Stankevich, V.K., and Trofimov, B.A., *Nauka Proizvodstvu,* 2003, no. 6, p. 18.
41. Bentrude, W.G. and Setzer, W.N., *Geminal Proton-Phosphorus Couplings, $^2J(PH)$. In Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis Organic Compounds and Metal Complexes,* Verkade, J.G. and Quin, D., Eds., Deerfield Beach: VCH Publ., 1987, vol. 8, p. 380.