Synthesis and transformations of metallacycles
40.* Catalytic cycloalumination in the synthesis of 3-substituted phospholanes

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An efficient one-pot method was developed for the synthesis of 3-alkyl- and 3-benzyl-substituted phospholanes through the successive Cp_2ZrCl_2-catalyzed cycloalumination of α-olefins in the presence of $AlEt_3$ giving the corresponding aluminacyclopentanes followed by the *in situ* replacement of the aluminum atom in the latter compounds by a P atom by means of methyl(phenyl)dichlorophosphines. The oxidation of 3-alkyl- and 3-benzyl-1-methyl(phenyl)-phospholanes with hydrogen peroxide affords 3-alkyl- and 3-benzyl-1-methyl(phenyl)-phospholane 1-oxides, respectively.

Key words: aluminacyclopentanes, dichlorophosphines, phospholanes, heterocycles, metal complex catalysis, organoaluminum compounds, zirconium complexes.

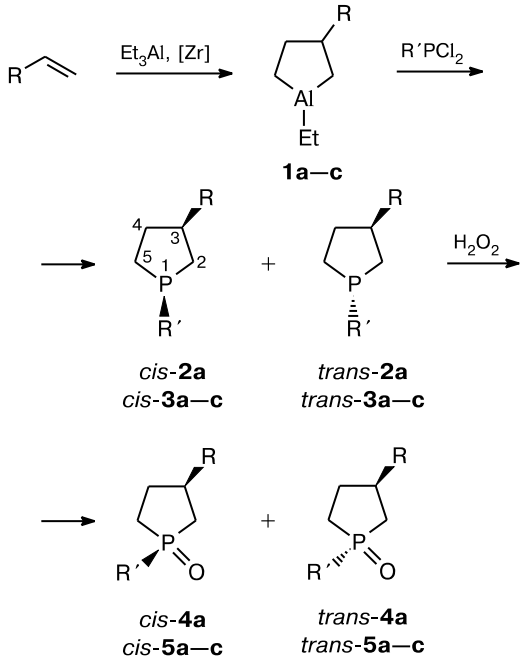
Phosphorus-containing heterocycles have attracted firm interest from chemists due to their unique properties. Great attention paid to this class of compounds is associated with their use as intermediates in multistep organic synthesis,[2,3] ligands for catalytic systems,[4—6] and efficient agents for medicine and agriculture.[7] Hence, the development of new preparative methods for the synthesis of phospholanes and their derivatives is of considerable interest.

A fairly large number of approaches to cyclic ogranophosphorus compounds (OPC) are available in the literature. Reactions of trivalent phosphorus halides with dienes, α,β-unsaturated carbonyl compounds, imines, and 1,2-diketones are known.[8,9] One of the promising approaches to the synthesis of five-membered phosphorus-containing heterocycles is based on direct transformations of metallacarbocycles into cyclic OPC.[10,11] However, this method requires the use of stoichiometric amounts of expensive π complexes based on Zr, Ti, Hf, and Co and is difficult to accomplish. In particular, these reactions should be performed at low temperature (from −90 to −78 °C), due to which this method has little practical application in modern organic and organometallic synthesis.

The purpose of the present study was to extend the scope of catalytic cycloalumination of unsaturated compounds[12,13] in the synthesis of phospholanes starting from 3-substituted aluminacyclopentanes, which are prepared *in situ* by the reaction of α-olefins with Et_3Al in the presence of Cp_2ZrCl_2, and phosphorus alkyl- or aryldihalides.

Initially, we chose 3-benzyl-1-ethylaluminacyclopentane (**1a**) as a model compound. We found that the *in situ* reaction of aluminacyclopentane **1a** with methyldichlorophosphine is accompanied by the replacement of the Al atom by a P atom to form 3-benzyl-1-methylphospholane (**2a**) in 84% yield (Scheme 1).

Scheme 1



[Zr] = Cp_2ZrCl_2
R = Bn (**a**), Bu (**b**), Hex (**c**)
R´ = Me (**2a**, **4a**), Ph (**3a**—**c**, **5a**—**c**)

* For Part 39, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1540—1543, August, 2012.

The reaction of 3-benzyl-1-ethylaluminacyclopentane (**1a**) with phenyldichlorophosphine affords 3-benzyl-1-phenylphospholane (**3a**) in 82% yield.

Under the conditions used, 3-alkyl-substituted aluminacyclopentanes **1b—c** react with phenyldichlorophosphine to form 3-butyl-1-phenylphospholane (**3b**) and 3-hexyl-1-phenylphospholane (**3c**) in 92 and 91% yields, respectively.

The synthesized phospholanes **2a** and **3a—c** readily react with H_2O_2 in chloroform to give phospholane 1-oxides **4a** and **5a—c**, respectively, in quantitative yields.

The ^1H and ^{13}C NMR spectra of the synthesized compounds show a double set of signals associated with the presence of two stereoisomers, which are formed due to the high barrier to inversion of configuration at the phosphorus atom.[14] The *cis* to *trans* isomer ratio varies depending on the structure of the substituent at the phosphorus atom. Thus, there is a large difference in the integrated intensities of the signals in the ^{13}C NMR spectrum of methyl-substituted compound **2a**, the ratio being equal to 2 : 1. The assignment of the signals for each isomer of 3-benzyl-1-methylphospholane (**2a**) was made based on the results of 2D NMR spectroscopy (HSQC, COSYHH, HMBC). It was found that all signals of the major component of the mixture are at lower field compared to the minor component. The exceptions are the chemical shifts of the carbon atoms in position 4, for which the reverse order of the signals is observed. The largest difference $\Delta\delta = \delta_{trans} - \delta_{cis} = 2.4$ ppm was found for the bridgehead carbon atoms C(3). The ^{31}P NMR spectrum shows the following two signals: a lower-intensity signal at δ 35.0 and a higher-intensity signal at δ −34.4 corresponding to the region of tertiary phosphines.[15] The presence of the phosphorus atom in the five-membered ring causes doublet splitting of the signals for α-, β-, and γ-carbon atoms in the ^{13}C NMR spectrum with the corresponding constants $^1J_{P,C}$, $^2J_{P,C}$, and $^3J_{P,C}$. The largest value of the spin-spin coupling constant was observed for the CH_3 group at the phosphorus atom ($J_{P,C} = 28.4$ Hz for both isomers), whereas the coupling constants for the C(2) and C(5) atoms with the phosphorus atom are 14.2—17.2 and 11.1—14.2 Hz, respectively. The replacement of the methyl substituent by a phenyl group leads to an increase in the spin-spin coupling constant to 15.8—20.5 Hz for C(2) and 14.2—20.0 Hz for C(5) for compounds **3a—c**. In this case, the chemical shift of the phosphorus atom in these compounds also substantially changes (to −14.1 to −12.6 ppm). In oxidized phosphacyclopentanes **4a** and **5a—c**, the endocyclic α-carbon atoms C(2) and C(5) have $^1J_{P,C} \approx 88$—101 Hz. In the ^{31}P NMR spectra of compounds **4a** and **5a—c**, the signals are shifted in the positive direction to ~59—67 ppm, which is consistent with the literature data.[15] The assignment of signals in the ^1H, ^{13}C, and ^{31}P NMR spectra of 3-benzyl-1-methylphospholane 1-oxide (**4a**), 3-alkyl- and 3-benzyl-1-phenylphospholane 1-oxides (**5a—c**) was also made based on the 2D homo- and heteronuclear correlation spectra (COSYHH, HSQC, C—H HMBC, P—H HMBC). The stereochemistry of the isomers was determined based on the results of quantum chemical calculations (PBE/3ξ and MP2) of the relative thermodynamic parameters ($\Delta G_{отн}$) for all synthesized phospholanes ($\Delta G_{cis} > \Delta G_{trans}$ by 0.5—1.5 kcal mol^{-1}).[16] Actually, the upfield shifts of the signals of the carbon atoms (for example, in compound *cis*-**2a**) for P—$\underline{C}H_3$ and $\underline{C}H_2Ph$ can be attributed to the intramolecular 1-4-*syn* interaction between these groups of atoms.

Therefore, the replacement of the aluminum atom by phosphorus in five-membered aluminacarbocycles is an efficient tool for the construction of cyclic organophosphorus compounds in one preparative step. In the nearest future, this approach will be used in the synthesis of phosphacyclopentanes with different structures, as well as of macrocyclic di- and polyphosphorus compounds.

Experimental

The chromatographic analysis was performed on a Shimadzu GC-9A instrument; a 2000×2 mm column; stationary phase SE-30 silicone (5%) on Chromaton N-AW-HMDS (0.125—0.160 mm); helium as the carrier gas (30 mL min^{-1}); temperature programming from 50 to 300 °C at a rate of 8 °C min^{-1}. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance-400 spectrometer (100.58 MHz for ^{13}C, 400.00 MHz for ^1H, and 161.92 MHz for ^{31}P) in $CDCl_3$. The positive-ion mass spectra were obtained in the reflection mode on a MALDI TOF/TOF Autoflex-III Bruker instrument using 2,5-dihydrobenzoic acid (2,5-DHB) and α-cyano-4-hydroxycinnamic acid (HCCA) as the matrix. Elemental analyses were carried out on a Karlo Erba elemental analyzer, model 1106. Thin-layer chromatography was performed on Silufol UV-254 plates using a 5 : 3 : 1 hexane—ethyl acetate—methanol system; the visualization was performed with I_2. The column chromatography was carried out using silica gel (Acros, 0.060—0.200 mm). The yields of the products were determined by GLC using undecane as the internal standard. The isomer ratio was estimated from the intensities of the signals in the ^1H and ^{13}C NMR spectra. The reactions with organometallic compounds were performed under a stream of dry argon. The solvents were dried and distilled immediately before use; Cp_2ZrCl_2 was synthesized according to a known procedure.[17] Commercial phosphines (Acros) and Et_3Al (92%) (Redkino pilot-production plant) were used.

Synthesis of 3-alkyl- and 3-benzyl-1-methyl(phenyl)phospholanes (general procedure). Toluene (25 mL), Cp_2ZrCl_2 (0.298 g, 1 mmol), olefin (10 mmol), and $AlEt_3$ (1.8 mL, 12 mmol) were sequentially placed in a glass reactor with stirring under a dry argon atmosphere at 0 °C. The temperature was brought to room temperature (~20 °C), and the reaction mixture was stirred for 12 h. Then the reaction mixture was cooled to −10 or −15 °C, after which methyl- or phenyldichlorophosphine (12 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 30 min and worked-up with a saturated NH_4Cl aqueous solution. The reaction products were extracted with diethyl ether and dried over $MgSO_4$. The solvent was evaporat-

ed, and the target phospholanes were isolated by distillation *in vacuo*. All operations were carried out under a stream of argon.

Synthesis of 3-alkyl- and 3-benzyl-1-methyl(phenyl)phospholane 1-oxides (general procedure). A 30% hydrogen peroxide solution (0.7 mL, 6 mmol) was slowly added dropwise with vigorous stirring to a solution of 3-alkyl- or 3-benzyl-1-alkyl(phenyl)phospholane (5 mmol), which were synthesized according to the above-described procedure, in chloroform (10 mL). The reaction mixture was stirred for 1 h and washed with water (3×5 mL), the organic layer was dried over $MgSO_4$, the solvent was evaporated, and the residue was chromatographed on silica gel (hexane : ethyl acetate : methanol = 5 : 3 : 1).

3-Benzyl-1-methylphospholane (2a) (*trans* : *cis* = 2 : 1). Yield 84%. B.p. 121—125 °C (6 Torr). Found (%): C, 75.6; H, 8.8. $C_{12}H_{17}P$. Calculated (%): C, 74.97; H, 8.91. ^{1}H NMR, δ, *trans* isomer: 1.06 (m, 4 H, PC(6)H_3, C(2)H_a); 1.48—1.68 (m, 3 H, C(4)H_a, C(5)H_2); 1.98—2.20 (m, 3 H, C(3)H, C(2)H_b, C(4)H_b); 2.80 (t, 2 H, C(1´)H_2, ^3J = 5.8 Hz); 7.20—7.25, 7.30—7.35 (m, 5 H, Ph); *cis* isomer: 1.00—1.03 (m, 3 H, PC(6)H_3); 1.32—1.42 (m, 3 H, C(2)H_a, C(4)H_a, C(5)H_a); 2.0—2.15 (m, 3 H, C(2)H_b, C(4)H_b, C(5)H_b); 2.38 (m, 1 H, C(3)H); 2.68 (dd, 1 H, C(1´)H_a, ^2J = 12 Hz, ^3J = 7.3 Hz); 2.72 (dd, 1 H, C(1´)H_b, ^2J = 12 Hz, ^3J = 7.3 Hz); 7.20—7.25, 7.30—7.35 (m, 5 H, Ph). ^{13}C NMR, δ, *trans* isomer: 14.24 (C(6), $J_{P,C}$ = 28.4 Hz); 26.80 (C(5), $J_{P,C}$ = 11.1); 33.08 (C(4), $J_{P,C}$ = 6.3 Hz); 34.20 (C(2), $J_{P,C}$ = 17.4 Hz); 42.75 (C(1´), $J_{P,C}$ = 7.9 Hz); 45.56 (C(3), $J_{P,C}$ = 3.2 Hz); 125.87, 128.28, 128.80, 141.66 (Ph); *cis* isomer: 13.94 (C(6), $J_{P,C}$ = 28.4 Hz); 26.69 (C(5), $J_{P,C}$ = 14.2 Hz); 33.60 (C(2), $J_{P,C}$ = 14.2 Hz); 34.18 (C(4), $J_{P,C}$ = 3.2 Hz); 41.94 (C(1´), $J_{P,C}$ = 4.7 Hz); 43.16 (C(3), $J_{P,C}$ = 7.9 Hz); 125.87, 128.28, 128.87, 141.66 (Ph). ^{31}P NMR, δ, *trans* isomer: −34.41; *cis* isomer: −35.07. MS (MALDI TOF/TOF), found: *m/z* 192.998 $[M + H]^+$. $C_{12}H_{17}PH$. Calculated: M = 192.107.

3-Benzyl-1-phenylphospholane (3a) (*trans* : *cis* = 3 : 2). Yield 82%. B.p. 198—202 °C (6 Torr). Found (%): C, 80.2; H, 7.6. $C_{17}H_{19}P$. Calculated (%):C, 80.29; H, 7.53. ^{1}H NMR, δ, *trans* isomer: 1.42—1.50 (m, 1 H, C(4)H_a); 1.63—1.73 (m, 1 H, C(2)H_a); 1.83—1.91 (m, 1 H, C(5)H_a); 2.02—2.12 (m, 2 H, C(4)H_b, C(5)H_b); 2.24 (m, 1 H, C(3)H); 2.30—2.40 (m, 1 H, C(2)H_b); 2.75 (d, 1 H, C(1´)H_a); 2.77 (d, 1 H, C(1´)H_b, J = 4.3 Hz); 7.15—7.47 (m, 10 H, Ar); *cis* isomer: 1.42—1.50 (m, 1 H, C(4)H_a); 1.61 (m, 1 H, C(2)H_a); 1.93—1.99 (m, 1 H, C(5)H_a); 2.02—2.12 (m, 2 H, C(2)H_b, C(4)H_b); 2.20—2.30 (m, 2 H, C(5)H_b); 2.32 (m, 1 H, C(3)H); 2.72 (d, 2 H, C(1´)H_2); 7.15—7.47 (m, 10 H, Ar). ^{13}C NMR, δ, *trans* isomer: 25.88 (C(5), $J_{P,C}$ = = 20 Hz); 33.15 (C(2), $J_{P,C}$ = 20 Hz); 33.95 (C(4), $J_{P,C}$ = 7.9 Hz); 41.99 (C(1´), $J_{P,C}$ = 4.7 Hz); 43.79 (C(3), $J_{P,C}$ = 7.9 Hz); 125.90, 128.30, 128.85, 141.34 (CH_2Ph); 127.31, 128.30, 130.39 ($J_{P,C}$ = 25.3 Hz); 142.42 ($J_{P,C}$ = 34.8 Hz) (PPh); *cis* isomer: 26.54 (C(5), $J_{P,C}$ = 15.8 Hz); 32.99 (C(2), $J_{P,C}$ = 20.5 Hz); 34.27 (C(4), $J_{P,C}$ = 4.7 Hz); 42.15 (C(1´), $J_{P,C}$ = 7.9 Hz); 45.01 (C(3)); 125.92, 128.30, 128.82, 141.45 (CH_2Ph); 127.31, 128.30, 130.45 ($J_{P,C}$ = 23.7 Hz), 142.97 ($J_{P,C}$ = 36.3 Hz) (PPh). ^{31}P NMR, δ, *trans*- and *cis* isomers: −13,58. MS (MALDI TOF/TOF), found: *m/z* 255.432 $[M + H]^+$. $C_{17}H_{19}PH$. Calculated: M = 254.122.

3-Butyl-1-phenylphospholane (3b) (*trans* : *cis* = 3 : 2). Yield 92%. B.p. 172—177 °C (10 Torr). Found (%): C, 76.3; H, 9.8. $C_{14}H_{21}P$. Calculated (%): C, 76.33; H, 9.61. ^{1}H NMR, δ, *trans* isomer: 0.91 (t, 3 H, C(4´)H_3, ^3J = 7.2 Hz); 1.26—1.41 (m, 5 H, C(2´,3´)H_2, C(4)H_a); 1.37—1.60 (m, 3 H, C(1´)H_2, C(2)H_a); 1.85—2.00 (m, 2 H, C(3)H, C(5)H_a); 2.05—2.19 (m, 1 H, C(4)H_b); 2.19—2.33 (m, 1 H, C(5)H_b); 2.39 (dd, 1 H, C(2)H_b, ^2J = 13.3 Hz, ^3J = 7.2 Hz); 7.28, 7.34, 7.40—7.48 (m, 5H, Ph); *cis* isomer: 0.91 (t, 3 H, C(4´)H_3, ^3J = 7.2 Hz); 1.26—1.39 (m, 5 H, C(2´,3´)H_2, C(4)H_a); 1.39—1.58 (m, 3 H, C(1´)H_2, C(2)H_a); 1.84—1.99 (m, 2 H, C(3)H, C(5)H_a); 2.02—2.19 (m, 2 H, C(4)H_b, C(5)H_b); 2.45 (dd, 1 H, C(2)H_b, ^2J = 12.9 Hz, ^3J = 7.5 Hz); 7.28, 7.34, 7.40—7.48 (m, 5 H, Ph). ^{13}C NMR, δ, *trans* isomer: 14.10 (C(4´)); 22.94 (C(3´)); 26.00 (C(5), $J_{P,C}$ = 17.4 Hz); 30.98 (C(2´)); 33.32 (C(2), $J_{P,C}$ = 15.8 Hz); 34.18 (C(4)); 35.53 (C(1´), $J_{P,C}$ = 4.7 Hz); 43.22 (C(3)); 127.33, 128.28, 130.42 ($J_{P,C}$ = = 23.7 Hz), 142.30 ($J_{P,C}$ = 36.3 Hz) (Ph); *cis* isomer: 14.10 (C(4´)); 22.87 (C(3´)); 26.75 (C(5), $J_{P,C}$ = 12.6 Hz); 31.06 (C(2´)); 33.07 (C(2), $J_{P,C}$ = 15.8 Hz); 33.48 (C(4), $J_{P,C}$ = 6.3 Hz); 35.80 (C(1´), $J_{P,C}$ =6.3 Hz); 42.09 (C(3), $J_{P,C}$ = 6.3 Hz); 127.37, 128.23, 130.50 ($J_{P,C}$ = 23.7 Hz), 142.51 ($J_{P,C}$ = 36.3 Hz) (Ph). ^{31}P NMR, δ, *trans*- and *cis* isomers: −12.55. MS (MALDI TOF/TOF), found: *m/z* 221.331 $[M + H]^+$. $C_{12}H_{17}PH$. Calculated: M = 220.138.

3-Hexyl-1-phenylphospholane (3c) (*trans* : *cis* = 3 : 2). Yield 91%. B.p. 191—194 °C (9 Torr). Found (%): C, 77.3; H, 10.2. $C_{16}H_{25}P$. Calculated (%): C, 77.38; H, 10.15. ^{1}H NMR, δ, *trans* isomer: 0.93 (t, 3 H, C(6´)H_3, ^3J = 7.2 Hz); 1.26—1.40 (m, 10 H, C(1´)H_2, C(2´)H_2, C(3´)H_2, C(4´)H_2, C(5´)H_2); 1.41—1.62 (m, 2 H, C(2)H_a, C(4)H_a); 1.84—2.01 (m, 2 H, C(3)H, C(5)H_a); 2.13—2.20 (m, 1 H, C(4)H_b); 2.20—2.32 (m, 1 H, C(5)H_b); 2.39 (dd, 1 H, C(2)H_b, ^2J = 13.3 Hz, ^3J = 7.2 Hz); 7.28, 7.35, 7.40—7.48 (m, 5 H, Ph); *cis* isomer: 0.93 (t, 3 H, C(6´)H_3, ^3J = 7.2 Hz); 1.27—1.50 (m, 10 H, C(1´)H_2, C(2´)H_2, C(3´)H_2, C4´)H_2, C(5´)H_2); 1.50—1.61 (m, 2 H, C(2)H_a, C(4)H_a); 1.83—2.01 (m, 2 H, C(3)H, C(5)H_a); 2.02—2.22 (m, 2 H, C(4)H_b, C(5)H_b); 2.45 (dd, 1 H, C(2)H_b, ^2J = 12.9 Hz, ^3J = 7.5 Hz); 7.28, 7.35, 7.40—7.48 (m, 5 H, Ph). ^{13}C NMR, δ, *trans* isomer: 14.10 (C(6´)); 22.66 (C(5´)); 26.06 (C(5), $J_{P,C}$ = 17.4 Hz); 28.72 (C(2´)); 29.56 (C(3´)); 31.85 (C(4´)); 33.43 (C(2); $J_{P,C}$ = 17.4 Hz); 34.21 (C(4), $J_{P,C}$ = 3.2 Hz); 35.87 (C(1´), $J_{P,C}$ = 6.3 Hz); 43.28 (C(3)); 127.17, 128.21, 130.36 ($J_{P,C}$ = 23.7 Hz), 142.73 ($J_{P,C}$ = = 36.3 Hz) (Ph); *cis* isomer: 14.10 (C(6´)); 22.66 (C(5´)); 26.86 (C(5), $J_{P,C}$ = 14.2 Hz); 28.83 (C(2´)); 29.50 (C(3´)); 31.85 (C(4´)); 33.19 (C(2), $J_{P,C}$ = 20.5 Hz); 34.52 (C(4), $J_{P,C}$ = 6.3 Hz); 36.13 (C(1´), $J_{P,C}$ = 7.9 Hz); 42.10 (C(3), $J_{P,C}$ = 6.3 Hz); 127.17, 128.17, 130.42 ($J_{P,C}$ = 25.3 Hz), 143.09 ($J_{P,C}$ = 34.8 Hz) (Ph). ^{31}P NMR, δ, *trans* isomer: −13.74; *cis* isomer: −14.12. MS (MALDI TOF/TOF), found: *m/z* 249.166 $[M + H]^+$. $C_{12}H_{17}PH$. Calculated: M = 248.169.

3-Benzyl-1-methylphospholane 1-oxide (4a) (*trans* : *cis* = = 2 : 1). R_f = 0.71. Found (%): C, 60.4; H, 8.3. $C_{12}H_{17}OP$. Calculated (%): C, 60.21; H, 8.23. ^{1}H NMR, δ, *trans* isomer: 1.20—1.23 (m, 1 H, C(5)H_a); 1.23—1.31 (m, 1 H, C(2)H_a); 1.62 (s, 3 H, PC(6)H_3); 1.68—1.72 (m, 1 H, C(4)H_a); 1.99—2.10 (m, 3 H, C(2)H_b, C(4)H_b, C(5)H_b); 2.51 (1 H, C(3)H, ^3J = 6); 2.69 (d, 2 H, C(1´)H_2, J = 8.0 Hz); 7.13—7.17, 7.21—7.26 (m, 5 H, Ph); *cis* isomer: 1.20—1.30 (m, 2 H, C(2)H_a, C(5)H_a); 1.66 (s, 3 H, PC(6)H_3); 1.67—1.72 (m, 1 H, C(4)H_a); 1.79—1.86 (m, 1 H, C(5)H_b); 2.00—2.16 (m, 3 H, C(3)H, C(2)H_b, C(4)H_b); 2.72 (d, 2 H, C(1´)H_2, J = 8.2 Hz); 7.21—7.26 (m, 5 H, Ph). ^{13}C NMR, δ *trans* isomer: 18.01 (C(6)); 30.24 (C(5); $J_{P,C}$ = = 107.4); 30.52 (C(4)); 34.21 (C(2), J = 107.4 Hz); 40.90 (C(3), J = 12.6 Hz); 42.24 (C(1´), $J_{P,C}$ = 22.1 Hz); 126.46, 128.59, 128.89, 139.59 (Ph); *cis* isomer: 17.39 (C(6)); 29.58 (C(5), $J_{P,C}$ = 107.4 Hz); 31.34 (C(4)); 35.14 (C(2); $J_{P,C}$ = 107.4 Hz); 40.67 (C(3), $J_{P,C}$ = 12.6 Hz); 42.17 (C(1´), $J_{P,C}$ = 22.1 Hz);

126.46, 128.59, 128.99, 139.84 (Ph). ^{31}P NMR, δ, *trans* isomer: 67.22; *cis* isomer: 67.73. MS (MALDI TOF/TOF), found: *m/z* 209.165 $[M + H]^+$. $C_{12}H_{17}PH$. Calculated: M = 208.102.

3-Benzyl-1-phenylphospholane 1-oxide (5a) (*trans* : *cis* = = 3 : 2). R_f = 0.42. Found (%): C, 75.7; H, 7.2. $C_{17}H_{19}OP$. Calculated (%): C, 75.54; H, 7.08. ^{1}H NMR, δ, *trans* isomer: 1.54—1.63 (m, 1 H, C(2)H_a); 1.89—1.96 (m, 1 H, C(5)H_a); 2.07—2.27 (m, 4 H C(2)H_b, C(4)H_2, C(5)H_b); 2.30—2.36 (m, 1 H, C(3)H); 2.75 (d, 2 H, C(1′)H_2, J = 6,4 Hz); 7.15—7.25, 7.30 (m, 5 H, CH_2Ph); 7.45—7.55, 7.71 (m, 5 H, PPh); *cis* isomer: 1.42—1.51 (m, 1 H, C(4)H_a); 1.79—1.88 (m, 1 H, C(2)H_a); 1.89—1.96 (m, 1 H, C(5)H_a); 2.07—2.27 (m, 2 H, C(2)H_b, C(5)H_b); 2.30—2.36 (m, 1 H, C(4)H_b); 2.73 (m, 1 H, C(3)H); 2.78 (d, 2 H, C(1′)H_2, J = 6 Hz); 7.15—7.25, 7.30 (m, 5 H, CH_2Ph); 7.45—7.55, 7.71 (m, 5 H, PPh). ^{13}C NMR, δ, *trans* isomer: 30.42 (C(5), $J_{P,C}$ = 104.3 Hz); 30.75 (C(4), $J_{P,C}$ = 7.9 Hz); 35.57 (C(2), $J_{P,C}$ = 94.8 Hz); 41.89 (C(3), $J_{P,C}$ = 12.6 Hz); 42.34 (C(1′), $J_{P,C}$ = 20 Hz); 126.16, 128.32, 128.66, 139.58 (CH_2Ph); 128.54, 128.66, 129.69, 131.51 (PPh); *cis* isomer: 29.42 (C(5), $J_{P,C}$ = 104.3 Hz); 31.82 (C(4), $J_{P,C}$ = 7.9 Hz); 36.20 (C(2), $J_{P,C}$ = 91.6 Hz); 40.58 (C(3), $J_{P,C}$ = 12.6 Hz); 42.22 (C(1′), $J_{P,C}$ = 20 Hz); 126.18, 128.28, 128.66, 139.26 (CH_2Ph); 128.43, 128.66, 129.69, 131.53 (PPh). ^{31}P NMR, δ, *trans* isomer: 59.48; *cis* isomer: 58.87. MS (MALDI TOF/TOF), found: *m/z* 271.331 $[M + H]^+$. $C_{17}H_{19}OPH$. Calculated: M = 270.117.

3-Butyl-1-phenylphospholane 1-oxide (5b) (*trans* : *cis* = 3 : 2). R_f = 0.35. Found (%): C, 71.2; H, 8.0. $C_{14}H_{21}OP$. Calculated (%): C, 71.16; H, 8.96. ^{1}H NMR, δ, *trans* isomer: 0.91 (t, 3 H, C(4′)H_3, ^3J = 7.2 Hz); 1.29—1.39 (m, 4 H, C(2′)H_2, C(3′)H_2); 1.47—1.58 (m, 3 H, C(1′)H_2, C(2)H_a); 1.70 (m, 1 H, C(5)H_a); 1.75—1.83 (m, 1 H, C(4)H_a); 2.00 (m, 1 H, C(3)H); 2.14—2.26 (m, 3 H, C(2)H_b, C(4)H_b, C(5)H_b); 7.45—7.56, 7.68—7.77 (m, 5 H, Ph); *cis* isomer: 0.91 (t, 3 H, C(4′)H_3, ^3J = 7.2 Hz); 1.29—1.39 (m, 5 H, C(2′)H_2, C(3′)H_2, C(4)H_a); 1.40—1.58 (m, 2 H, C(1′)H_2); 1.67—1.73 (m, 1 H, C(2)H_a); 2.09 (m, 1 H, C(5)H_a); 2.19 (m, 1 H, C(5)H_b); 2.22—2.41 (m, 3 H, C(3)H, C(2)H_b, C(4)H_b); 7.45—7.56, 7.68—7.77 (m, 5 H, Ph). ^{13}C NMR, δ, *trans* isomer: 14.07 (C(4′)); 22.49 (C(3′)); 29.32 (C(5), $J_{P,C}$ = = 104.3 Hz); 29.88 (C(2′)); 30.76 (C(4), $J_{P,C}$ = 9.5 Hz); 35.62 (C(2), $J_{P,C}$ = 88.5 Hz); 35.74 (C(1′), $J_{P,C}$ = 9.5 Hz); 39.95 (C(3), $J_{P,C}$ = 12.6 Hz); 128.61, 129.89, 131.66, 134.07 (PPh); *cis* isomer: 14.07 (C(4′)); 22.49 (C(3′)); 29.74 (C(2′)); 30.34 (C(5), $J_{P,C}$ = 104.3 Hz); 32.02 (C(4), $J_{P,C}$ = 9.5 Hz); 35.87 (C(1′), $J_{P,C}$ = 11.1 Hz); 36.30 (C(2), $J_{P,C}$ = 86.9 Hz); 38.68 (C(3), $J_{P,C}$ = 12.6 Hz); 128.72, 129.79, 131.66, 134.99 (PPh). ^{31}P NMR, δ, *trans* isomer: 60.11; *cis* isomer: 60.20. MS (MALDI TOF/TOF), found: *m/z* 237.413 $[M + H]^+$. $C_{12}H_{17}PH$. Calculated: M = 236.133.

3-Hexyl-1-phenylphospholane 1-oxide (5c) (*trans* : *cis* = 3 : 2). R_f = 0.44. Found (%): C, 72.7; H, 9.6. $C_{16}H_{25}OP$. Calculated (%): C, 72.70; H, 9.53. ^{1}H NMR, δ, *trans* isomer: 0.83 (t, 3 H, C(6′)H_3, ^3J = 7.2 Hz); 1.66—1.33 (m, 10 H, C(1′)H_2, C(2′)H_2, C(3′)H_2, C(4′)H_2, C(5′)H_2); 1.58—1.70 (m, 1 H, C(2)H_a); 1.70—1.80 (m, 1 H, C(4)H_a); 1.80—1.90 (m, 1 H, C(5)H_a); 1.90—2.01 (m, 1 H, C(3)H); 2.10—2.30 (m, 3 H, C(2)H_b, C(4)H_b, C(5)H_b); 7.36—7.50, 7.60—7.75 (m, 5 H, Ph); *cis* isomer: 0.83 (t, 3 H, C(6′)H_3, ^3J = 7.2 Hz); 1.16—1.33 (m, 11 H, C(1′)H_2, C(2′)H_2, C(3′)H_2, C(4′)H_2, C(5′)H_2, C(4)H_a); 1.37—1.53 (m, 1 H, C(2)H_a); 1.82—1.91 (m, 1 H, C(5)H_a); 2.06—2.15 (m, 1 H, C(5)H_b); 2.15—2.38 (m, 3 H, C(3)H, C(2)H_b, C(4)H_b); 7.36—7.50, 7.60—7.75 (m, 5 H, Ph). ^{13}C NMR, δ, *trans* isomer: 13.88 (C(6′)); 22.31 (C(5′)); 27.59 (C(2′)); 29.05 (C(3′)); 29.86 (C(5); $J_{P,C}$ = 60 Hz); 31.00 (C(4), $J_{P,C}$ = = 11.1 Hz); 31.47 (C(4′)); 35.65 (C(2), $J_{P,C}$ = 88.5 Hz); 36.02 (C(1′), $J_{P,C}$ = 6.3 Hz); 39.91 (C(3), $J_{P,C}$ = 14.2 Hz); 128.31, 129.54, 131.30, 134.23 (PPh); *cis* isomer: 13.80 (C(6′)); 22.31 (C(5′)); 27.48 (C(2′)); 28.99 (C(3′)); 29.20 (C(5), $J_{P,C}$ = 66.4 Hz); 30.73 (C(4), $J_{P,C}$ = 7.9 Hz); 31.47 (C(4′)); 36.14 (C(1′), $J_{P,C}$ = = 6.3 Hz); 36.32 (C(2), $J_{P,C}$ = 88.5 Hz); 38.64 (C(3), $J_{P,C}$ = = 12.6 Hz); 128.43, 129.64, 131.33, 134.16 (PPh). ^{31}P NMR, δ, *trans* isomer: 59.40; *cis* isomer: 59.50. MS (MALDI TOF/TOF), found: *m/z* 265.473 $[M + H]^+$. $C_{16}H_{25}OPH$. Calculated: M = 264.164.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 10-03-00046, 11-03-00103, and 11-03-97001).

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Received April 17, 2012;
in revised form June 9, 2012