Reaction of dibenzylphosphine oxide with α,β-unsaturated *O*-methyloximes

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The reaction of dibenzylphosphine oxide with *O*-methyloximes of some α,β-unsaturated ketones results in the phosphorylation at the β-carbon atom to form methoxyiminophosphine oxides, whereas the reaction of dibenzylphosphine oxide with *O*-methyloximes of α,β-unsaturated aldehydes affords aminodihydrophosphole oxides.

Key words: α,β-unsaturated oximes, dibenzylphosphine oxide, phosphorylation, phosphorus-containing heterocycles, phosphine oxides.

In the 1970s, Polish scientists showed the promising use of dibenzylphosphine oxide as a phosphorylating agent for olefins activated with respect to nucleophilic addition.[1,2] A great advantage of this reagent is its ability to afford, in some cases, derivatives of phosphorus-containing heterocycles, *viz.*, phospholanes. This possibility was demonstrated for unsaturated ketones and esters.

We succeeded to include α,β-unsaturated nitriles in the scope of substrates for this method of synthesis of phosphorus-containing heterocycles.[3,4] At the same time, nucleophilic addition of phosphorus reactants to derivatives of unsaturated carbonyl compounds, *viz.*, unsaturated oximes, remained virtually unstudied. A few published reactions of oximes with phosphorus reagents result, as a rule, in the reduction of the oxime group.[5,6]

We studied the reactions of dibenzylphosphine oxide with ethers of unsaturated ketoximes and aldoximes in the presence of sodium hydride. Evidently, it is senseless to introduce oximes themselves into this reaction, because they would form salts under these conditions, and their ability of adding nucleophiles would strongly decrease. This reaction turned out to be very sensitive to the substrate structure. For example, phosphorylation of ketoximes was successful only with pinocarvone *O*-methyloxime **1** and benzylideneacetone *O*-methyloxime **2** (Scheme 1). The double bond of pinocarvone oxime **1** is very accessible and favorable for the nucleophilic attack and, in the case of benzylideneacetone oxime **2**, the double bond is additionally activated by the phenyl group. Phosphine oxides **3** and **4**, respectively, were isolated as the reaction products. Attempts to involve oximes of other ketones in this reaction (carenone oxime **5** and carvone oxime **6**, oximes **7** and **8**) were unsuccessful, although the ketones themselves react readily with dibenzylphosphine oxide to form oxophosphine oxides: in the reaction, oximes **7** and **8** decomposed, and oximes **5** and **6** remained unchanged.

The structures of methoxyiminophosphine oxides **3** and **4** were proved by spectroscopic methods. The chemical shifts of signals for the phosphorus atom in the ^{31}P NMR spectra of compounds **3** and **4** indicate that phosphorus exists in the phosphine oxide form and is not incorporated in the ring. The ^{1}H and ^{13}C NMR spectra exhibit signals for the methoxy group, and the ^{13}C NMR spectrum contains a signal for the C=N—O fragment, proving that the methoxyimino group is retained in the molecules.

According to the data from the ^{1}H and ^{13}C NMR spectra, phosphine oxides synthesized from pinocarvone oxime **1** are epimeric derivatives of pinocamphone oxime **3** with a ratio of isomers of 3 : 1.

The signals in the ^{13}C and ^{1}H NMR spectra of **3** were assigned from the 2D ^{1}H—^{1}H and ^{13}C—^{1}H correlation spectra.

The configuration of the C(2) atom in the pinane skeleton was determined from comparison of the chemical shifts of the carbon atoms in compound **3** with the shifts for isopinocamphone oxime[7] and isomeric pinocamphone.[8] Based on this comparison, we concluded that the main isomer belongs to the isopinanocamphane series.

Phosphine oxide **4** was synthesized from benzylideneceтone oxime **2** as a mixture of *E*/*Z* isomers with respect to the oxime group in a ratio of 5 : 3 in favor of the *E* isomer (according to the ^{13}C NMR spectrum).

It is well known that the nucleophilic addition of phosphorus reagents to α,β-unsaturated aldehydes, unlike unsaturated ketones, occurs almost always on the carbonyl group.[9] Therefore, it was of interest to compare the reactivity of ethers of unsaturated ketoximes and aldoximes. For this purpose, we studied the reactions of dibenzylphosphine oxide with myrtenal (**9**), cinnamal (**10**), citral (**11**), and 2-methylpent-2-enal *O*-methyloximes (**12**) (Scheme 2).

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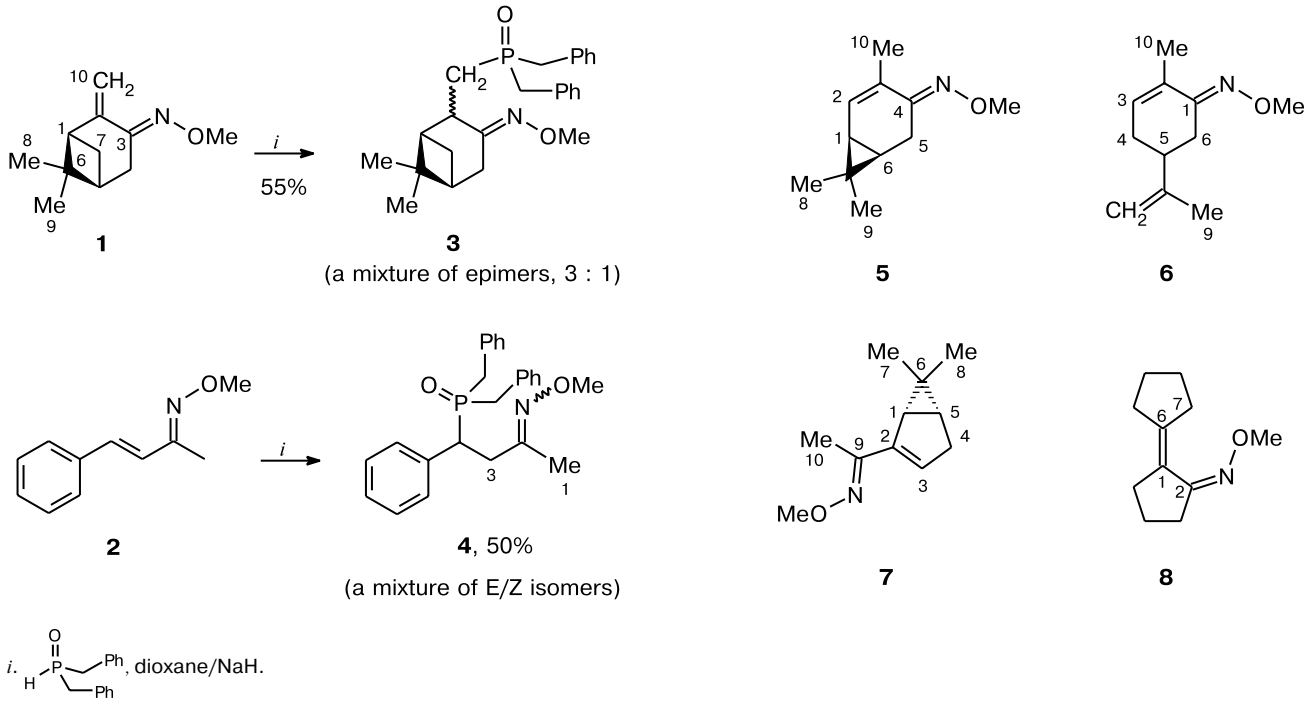
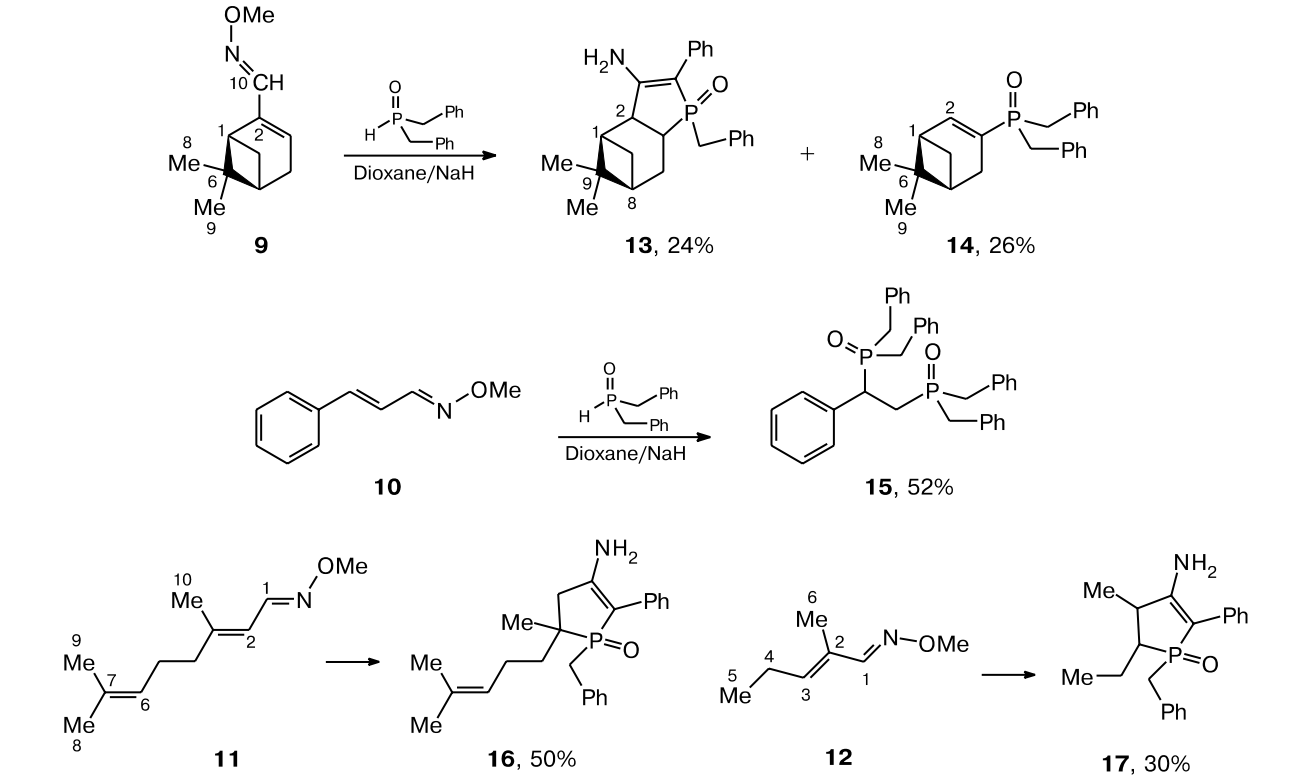
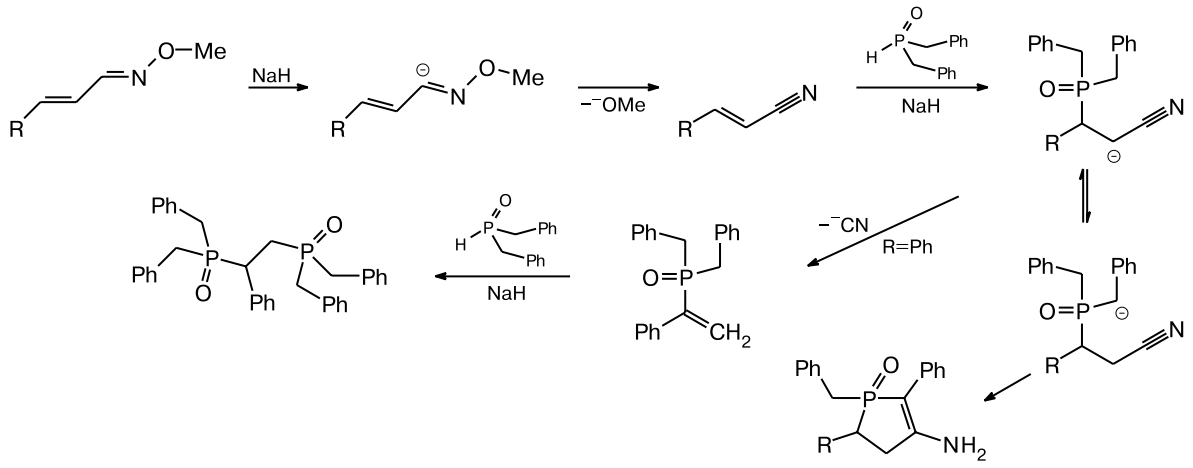
Scheme 1



Scheme 2



Scheme 3



The reactions of dibenzylphosphine oxide with these compounds do not afford methoxyimino derivatives of phosphine oxides. The products of the reactions of dibenzylphosphine oxide with citral (**11**) and 2-methylpent-2-enal *O*-methyloximes (**12**) are aminodihydrophosphole oxides **16** and **17**, respectively. The reaction with cinnamal *O*-methyloxime gave bisphosphine oxide **15**. Unsaturated phosphine oxide **14** is formed along with aminodihydrophosphole oxide **13** as the reaction product with myrtenal *O*-methyloxime (Scheme 2).

The structure of compound **14** was established by NMR spectroscopy. According to the elemental analysis and ^{13}C NMR spectroscopic data, one carbon atom is absent from the pinane framework. The chemical shift of the phosphorus atom indicates that phosphorus in the molecule is represented by phosphine oxide and is not incorporated into the ring. The ^{13}C NMR spectrum shows that the molecule contains the trisubstituted double bond with phosphorus as one of the substituents. The hydrogen atom is bound to another olefinic carbon atom. At the same time, the patterns of the ^{1}H and ^{13}C NMR spectra suggest that the pinane skeleton is retained on the whole.

It is noteworthy that aminodihydrophosphole oxides **13**, **16**, and **17** and bisphosphine oxide **15** have previously been synthesized by the reactions of dibenzylphosphine oxide with the corresponding nitriles.[3,4] This suggests the intermediate formation of nitriles from oxime ethers in the transformation under study. The plausible mechanism of the reaction of aldoxime ethers with dibenzylphosphine oxide is presented in Scheme 3.

According to this mechanism, sodium hydride induces the elimination of the methoxide anion to form unsaturated nitrile followed by the addition of dibenzylphosphine oxide. Further, two reaction routes become possible: (1) deprotonation of the methylene group of the benzyl fragment and attack of the benzyl anion followed by ring closure with the nitrile group to form aminodihydrophosphole oxide, and (2) elimination of the cyanide ion to form vinylphosphine oxide and the addition of the second equivalent of the phosphorus reagent to form bisphosphine oxide provided the substrate structure is favorable.

As can be seen, this scheme explains the formation of both aminodihydrophosphole oxides and unsaturated phosphine oxides along with bisphosphine oxide.

Thus, we have found that ethers of aliphatic and aromatic α,β-unsaturated ketoximes can react in some cases with dibenzylphosphine oxide in the presence of a base to form methoxyimino derivatives of phosphine oxides. The reactivity of α,β-unsaturated aldoxime ethers in the reaction with dibenzylphosphine oxide much exceeds that of unsaturated ketoximes. Unlike ketoximes, the reactions of aldoxime ethers produce aminodihydrophosphole oxides, phosphoolefins, or bisphosphine oxides.

Experimental

All solvents were distilled before use. Thin layer chromatography (TLC) was performed on Silufol plates with a fixed SiO_2 layer. To detect substances, the plates were sprayed with ethanolic solutions of vanillin (2 g of vanillin + 5 mL of conc. H_2SO_4 in 150 mL of EtOH) or iron chloride (10% solution of $FeCl_3 \cdot 6H_2O$ in EtOH) and heated. Silica gel (KSK, particle size 0.140—0.315 mm) activated at 140 °C for 6—7 h was used for column chromatography. IR spectra were recorded on a Bruker Vector-22 instrument. Mass spectra were obtained on a Finnigan MAT 8200 spectrometer (50—100 °C, EI, 70 eV). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 and 125.75 MHz) for solutions in $CDCl_3$ with concentrations of 70—100 mg mL^{-1} at 25—27 °C. The signals from the solvent were used as the internal standards: chloroform-d (δ_C = 76.90, δ_H = 7.24). ^{31}P NMR spectra were recorded under the same conditions on a Bruker AC-200 instrument (81.015 MHz, 80% H_3PO_4 as the external standard, δ_P 0.0). Signals were assigned using the ^{13}C NMR spectra recorded in the *J*-modulation regime (noise proton decoupling, opposite

phase for signals for atoms with even and odd numbers of attached protons with adjusting to the constant J = 135 Hz) and from data from the two-dimensional spectra: (1) ^{1}H—^{1}H homonuclear correlation, (2) ^{13}C—^{1}H heteronuclear correlation with direct spin-spin coupling constants (J = 135 Hz), and (3) ^{13}C—^{1}H heteronuclear correlation with long-range spin-spin coupling constants (J = 10 Hz). Optical rotations were measured on a Polamat A polarimeter for solutions in $CHCl_3$. Melting points were determined on a Koffler stage.

Synthesis of *O*-methyloximes (general procedure). To a solution of an oxime (0.02 mol) in benzene (70 mL), TEBAC (1—2 mg) and a 30% solution of NaOH (30 mL) were added. Dimethyl sulfate (0.03 mol) was added dropwise with intense stirring to the resulting mixture. The mixture was stirred at ~20 °C until the oxime disappeared (TLC monitoring). The reaction mixture was diluted with water (70 mL). The organic phase was separated and dried with sodium sulfate, and the solvent was distilled off. The resulting *O*-methyloxime was purified, if necessary, by percolation or distillation in a vacuum of an oil pump.

Pinocarvone (*E*)-*O*-methyloxime (1). High-resolution mass spectrum, found: m/z 179.13122. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (23), 164 (21), 148 (14), 136 (100), 104 (29), 91 (46), 79 (22), 77 (25), 69 (18), 53 (27). IR (in thin layer), ν/cm^{-1}: 2980—2810, 1050, 900, 820. ^{1}H NMR, δ: 0.74 (s, 3 H, H(8)); 1.12 (d, 1 H, H(7α), J = 9.2 Hz); 1.25 (s, 3 H, H(9)); 2.00 (m, 1 H, H(5)); 2.43—2.58 (m, 4 H, H(1), H(4), (7β)); 3.86 (s, 3 H, OMe); 4.60 (d, 1 H, H(10a), J = 2.0 Hz); 5.62 (d, 1 H, H(10b), J = 2.0 Hz). ^{13}C NMR, δ: 21.17 (C(8)); 26.21 (C(9)); 29.45 (C(4)); 31.31 (C(7)); 37.96 (C(5)); 40.43 (C(6)); 49.95 (C(1)); 61.64 (OMe); 107.74 (C(10)); 145.18 (C(2)); 152.38 (C(3)).

Benzylideneacetone *O*-methyloxime (2). The spectra of the sample were identical to the published data.[10]

2-Caren-4-one (*E*)-*O*-methyloxime (5), $[\alpha]^{24}_{578}$ +182.4 (c, 1.93). High-resolution mass spectrum, found: m/z 179.13160. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (36), 164 (30), 137 (73), 132 (32), 121 (17), 119 (23), 106 (100), 93 (52), 91 (52), 53 (13). IR (in thin layer), ν/cm^{-1}: 3000—2800, 1050, 900. ^{1}H NMR, δ: 0.76 (s, 3 H, H(8)); 0.99 (dd, 1 H, H(6), J = 8.1, 8.1 Hz); 1.10 (s, 3 H, H(9)); 1.11 (m, 1 H, H(1)); 1.79 (s, 3 H, H(10)); 2.48 (dd, 1 H, H(5α), J = 20.0, 8.5 Hz); 2.74 (d, 1 H, H(5β), J = 20.0 Hz); 3.82 (s, 3 H, OMe); 5.96 (d, 1 H, H(2), J = 4.5 Hz). ^{13}C NMR, δ: 13.85 (C(8)); 18.16 (C(10)); 18.62 (C(5)); 20.80 (C(6)); 23.16 (C(7)); 23.33 (C(1)); 27.85 (C(9)); 61.55 (OMe); 128.45 (C(3)); 129.81 (C(2)); 153.42 (C(4)).

Carvone (*E*)-*O*-methyloxime (6), $[\alpha]^{22}_{578}$ −13.3 (c 1.95). High-resolution mass spectrum, found: m/z 179.13122. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (62), 151 (12), 148 (39), 138 (100), 132 (34), 124 (13), 119 (28), 107 (99), 105 (74), 93 (40), 91 (61), 79 (67), 55 (50), 53 (79), 41(68). IR (in thin layer), ν/cm^{-1}: 3100—2750, 1650, 1450, 1370, 1052, 900. ^{1}H NMR, δ: 1.72 (s, 3 H, H(10)); 1.79 (s, 3 H, H(9)); 1.83—2.38 (m, 4 H, H_{ax}(4), H_{eq}(4), H(5), H_{ax}(6)); 3.07 (ddd, 1 H, H_{eq}(6), J = 16.5, 5.5, 1.7 Hz); 3.84 (s, 3 H, OMe); 4.72 (m, 2 H, H(8), $W_{1/2}$ = 2.7); 5.91 (m, 1 H, H(3), $W_{1/2}$ = 10.9). ^{13}C NMR, δ: 17.65 (C(10)); 20.74 (C(9)); 27.85 (C(4) or C(6)); 30.36 (C(4) or C(6)); 40.43 (C(5)); 61.47 (OMe); 110.02 (C(8)); 130.90 (C(2)); 131.36 (C(3)); 147.70 (C(7)); 155.28 (C(8)).

2-Acetyl-6,6-dimethylbicyclo[3.1.0]hex-2-ene *O*-methyloxime (7), $[\alpha]^{22}_{578}$ +8.6 (c 21.28). High-resolution mass spectrum, found: m/z 179.13086. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (70), 164 (97), 148 (80), 132 (72), 118 (24), 107 (42), 91 (100), 79 (33), 65 (26), 42 (30). IR (in thin layer), ν/cm^{-1}: 3100—2700, 1450, 1370, 1270, 1050, 900, 870, 790. ^{1}H NMR, δ: 0.75 (s, 3 H, H(7)); 1.08 (s, 3 H, H(8)); 1.27 (ddm, 1 H, H(5), J = 6.4, 6.4 Hz); 1.89 (s, 3 H, H(10)); 2.04 (dd, 1 H, H(1), J = 6.4, 3.2 Hz); 2.15 (dm, 1 H, H(4a), J = 19.0 Hz); 2.52 (ddd, 1 H, H(4b), J = 19.0, 7.3, 3.0 Hz); 3.87 (s, 3 H, OMe); 5.73 (m, 1 H, H(3)). ^{13}C NMR, δ: 11.57 (C(10)); 12.87 (C(7)); 18.73 (C(6)); 26.47 (C(8)); 28.36 (C(5)); 32.52 (C(4)); 36.05 (C(1)); 61.49 (OMe); 132.35 (C(3)); 141.80 (C(2)); 152.50 (C(9)).

1,1′-Bi(cyclopentyliden)-2-one *O*-methyloxime (8). High-resolution mass spectrum, found: m/z 179.13122. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (52), 153 (27), 148 (100), 120 (88), 105 (13), 94 (28), 91 (30), 81 (12), 79 (28), 77 (19), 53 (15). IR (in thin layer), ν/cm^{-1}: 3000—2800, 1420, 1050, 870, 850. ^{1}H NMR, δ: 1.70 (m, 6 H, H(4), H(8), H(9)); 2.30 and 2.50 (both m, 4 H each, H(3), H(5), H(7), H(10)). ^{13}C NMR, δ: 22.13, 26.06, 27.06, 28.83, 31.44, 33.67, 33.78 (C(3), C(4), C(5), C(7), C(8), C(9), C(10)); 61.53 (OMe); 125.41 (C(1)); 144.09 (C(6)); 161.83 (C(2)).

Myrtenal *O*-methyloxime (9), $[\alpha]^{22}_{578}$ −34.1 (c 3.28). High-resolution mass spectrum, found: m/z 179.13104. $C_{11}H_{17}NO$. Calculated: M = 179.13101. MS, m/z (I_{rel}(%)): 179 (47), 148 (54), 136 (100), 132 (29), 121 (23), 105 (52), 95 (50), 91 (47), 79 (50), 77 (55), 67 (29), 55 (25), 53 (34), 41 (64). IR (in thin layer), ν/cm^{-1}: 3000—2800, 1680, 1620, 1450, 1050, 870. ^{1}H NMR, δ: 0.81 (s, 3 H, H(8)); 1.14 (d, 1 H, H(7α), J = 9 Hz); 1.33 (s, 3 H, H(9)); 2.12 (m, 1 H, H(5)); 2.33—2.61 (m, 3 H, H(4), H(7β)); 2.82 (ddd, 1 H, H(1), J = 5.7, 5.7, 1.4 Hz); 3.79 (s, 3 H, OMe); 5.75 (m, 1 H, H(3)); 7.55 (s, 1 H, H(10)). ^{13}C NMR, δ: 20.98 (C(8)); 26.16 (C(9)); 31.18, 32.34 (C(7) and C(4)); 40.26 (C(6)); 40.46, 40.85 (C(1) и C(5)); 61.33 (OMe); 129.78 (C(3)); 143.34 (C(2)); 149.24 (C(10)).

Cinnamal *O*-methyloxime (10). The spectra of the sample are identical to the published data.[11]

3,7-Dimethylocta-2,6-dienal *O*-methyloxime (11). High-resolution mass spectrum, found: m/z 181.14609. $C_{11}H_{19}NO$. Calculated: M = 181.14666. MS, m/z (I_{rel}(%)): 181 (8), 113 (10), 82 (20), 69 (100), 53 (13), 41 (68). IR (in thin layer), ν/cm^{-1}: 3000—2800, 1720, 1650, 1440, 1380, 1050. ^{1}H NMR, δ: 1.58 and 1.66 (both s, 3 H each, H(8) and H(9)); 1.83 (s, 3 H, H(10)); 2.12 (m, 4 H, H(4), H(5)); 3.78 (s, 3 H, OMe); 5.04 (m, 1 H, H(6), $W_{1/2}$ = 10.3); 5.84 (dm, 1 H, H(2), J = 10 Hz); 7.88 (d, 1 H, H(1), J = 10 Hz). ^{13}C NMR, δ: 17.69 (C(9)); 24.15 (C(10)), 25.65 (C(8)); 26.78 (C(5)); 32.73 (C(4)); 61.21 (OMe); 118.48 (C(6)); 123.52 (C(2)); 131.78 (C(7)); 145.72 (C(3)); 146.54 (C(1)).

2-Methylpent-2-enal *O*-methyloxime (12). High-resolution mass spectrum, found: m/z 127.09971. $C_7H_{13}NO$. Calculated: M = 127.09971. MS, m/z (I_{rel}(%)): 127 (70), 112 (29), 100 (14), 96 (71), 94 (25), 81 (93), 69 (21), 67 (32), 55 (30), 53 (38), 41 (100). IR (in thin layer), ν/cm^{-1}: 3000—2800, 1460, 1060, 900. ^{1}H NMR, δ: 1.00 (t, 3 H, H(5), J = 7.5 Hz); 1.77 (m, 3 H, H(6), $W_{1/2}$ = 3); 2.17 (qdm, 2 H, H(4), J = 7.3 Hz, 7.3); 3.78 (s, 3 H, OMe); 5.59 (tm, 1 H, H(3), J = 7.3 Hz); 7.53 (s, 1 H, H(1)). ^{13}C NMR, δ: 11.32 (C(6)); 13.61 (C(5)); 21.42 (C(4)); 61.28 (OMe); 130.50 (C(2)); 139.43 (C(3)); 152.64 (C(1)).

Reaction of dibenzylphosphine oxide with *O*-methyloximes (general procedure). To a solution of dibenzylphosphine oxide (3.0 mmol) in anhydrous dioxane (25 mL), NaH (the content of NaH 60%, 6.0 mmol) was added. The reaction mixture was heated to boiling, and a solution of an *O*-methyloxime (2.0 mmol) in anhydrous dioxane (10 mL) was added dropwise with stirring. The mixture was refluxed with stirring until the initial oxime disappeared (TLC monitoring), cooled to ~20 °C, poured into a saturated solution of NaCl (100 mL), and extracted with ethyl acetate (50 mL). The extract was dried with Na_2SO_4 and the solvent was evaporated *in vacuo*. The residue was dried in a vacuum of an oil pump. The product was purified by flash chromatography or recrystallization.

10-(Dibenzylphosphinoylmethyl)isopinocamphone (*E*)-*O*-methyloxime (3a) and 10-(dibenzylphosphinoylmethyl)pinocamphone (*E*)-*O*-methyloxime (3b) (a mixture of C(2) isomers, 3 : 1) were isolated by chromatography of the product (1.15 g) prepared from pinocarvone *O*-methyloxime **1** (0.5 g, 2.8 mmol). The yield was 0.63 g (55%). White crystalline powder, m.p. 98—102 °C (from Bu^tOMe). High-resolution mass spectrum, found *m/z* 409.21775. $C_{25}H_{32}NO_2P$. Calculated: *M* = 409.21707. MS, *m/z* (I_{rel}(%)): 409 (23), 378 (31), 337 (14), 318 (23), 286 (11), 244 (7), 180 (26), 148 (53), 139 (18), 121 (9), 91 (100). IR (*c* = 2%, $CHCl_3$), ν/cm^{-1}: 3100—2800, 1600, 1450, 1245, 1050, 830. *Spectroscopic data for* **3a**. ^{31}P NMR, δ: 43.97. ^{1}H NMR, δ: 0.67 (s, 3 H, H(8)); 0.91 (d, 1 H, H(7α), *J* = 10.5 Hz); 1.11 (s, 3 H, H(9)); 1.72 (ddd, 1 H, H(10a), *J* = 15.2, 14.0, 9.0 Hz); 1.86 (m, 1 H, H(5)); 2.12 (m, 1 H, H(2)); 2.31 (ddd, 1 H, H(10b), *J* = 15.3, 6.8, 3.4 Hz); 2.35 (dddd, 1 H, H(7β), *J* = 10.5, 6.2, 6.2, 2.7 Hz); 2.47 (ddd, 1 H, H(4α), *J* = 18.8, 3.0, 3.0 Hz); 2.71 (dd, 1 H, H(4β), *J* = 18.8, 3.0 Hz); 2.81 (m, 1 H, C$\underline{H}_2$Ph); 3.03 (m, 1 H, C$\underline{H}_2$Ph); 3.10 (m, 1 H, H(1)); 3.26 (m, 2 H, C$\underline{H}_2$Ph); 3.86 (s, 3 H, OCH_3); 7.34—7.17 (m, 10 H, Ph). ^{13}C NMR, δ: 21.63 (C(8)); 26.90 (C(9)); 30.91 (C(10), $J_{C,P}$ = 64.2 Hz); 31.09 (C(4)); 32.97 (C(7)); 36.45 ($\underline{C}H_2$Ph, $J_{C,P}$ = 71.0 Hz); 36.52 ($\underline{C}H_2$Ph, $J_{C,P}$ = 69.6 Hz); 37.44 (C(5)); 38.37 (C(6)); 39.52 (C(1), $J_{C,P}$ = 3.2 Hz); 44.36 (C(2), $J_{C,P}$ = 2.2 Hz); 61.27 (OCH_3); 126.66 (C_p)); 128.43 and 128.53 (C_m); 129.83 ($J_{C,P}$ = 5.2 Hz), 129.93 ($J_{C,P}$ = 5.2 Hz) (C_o); 131.9 ($J_{C,P}$ = 7.3 Hz), 132.49 ($J_{C,P}$ = 6.9 Hz) (C_{ipso}); 159.30 (C(3), $J_{C,P}$ = 9.5 Hz). *Spectroscopic data for* **3b**. ^{31}P NMR, δ: 43.22. ^{1}H NMR, δ: 0.72 (s, H(8)); 0.84 (H(7α); 1.15 (s, H(9)); 2.17 (m, H(7β)); 3.84 (s, OCH_3). ^{13}C NMR, δ: 19.38 (C(8)); 26.29 (C(9)); 27.67 (C(7)); 37.11 (C(5)); 38.50 (C(6)); 43.67 (C(2)); 158.71 (C(3)) (*other signals of isomer* ***3a*** *are not seen because they overlap with the signals of the main isomer*).

4-Dibenzylphosphinoyl-4-phenylbutan-2-one *O*-methyloxime (4) (a mixture of *E*/*Z* isomers, 5 : 3) was isolated by recrystallization from benzene of the product (0.60 g) prepared from benzylideneacetone *O*-methyloxime **2** (0.30 g, 1.7 mmol). The yield was 0.34 g (50%). Yellowish crystals with m.p. 150—152 °C. High-resolution mass spectrum, found: *m/z* 405.18540. $C_{25}H_{28}NO_2P$. Calculated: *M* = 405.18577. MS, *m/z* (I_{rel}(%)): 405 (35), 374 (23), 314 (28), 176 (100), 144 (38), 139 (13), 121 (10), 104 (14), 103 (10), 91 (93), 65 (10). IR (*c* = 2%, $CHCl_3$), ν/cm^{-1}: 3100—2820, 1715, 1495, 1455, 1215, 1057, 730, 700, 670. ^{31}P NMR, δ: 44.19 (*E* isomer), 44.17 (*Z* isomer). ^{1}H NMR, δ: 1.34 (s, H(1), *Z* izomer); 1.48 (s, H(1), *E* isomer); 2.55—2.75 (m, H(3)); 2.76 and 3.04 (both m, C$\underline{H}_2$Ph); 3.35 (m, H(4), *Z* isomer); 3.38 (m, H(4), *E* isomer); 3.70 (s, OCH_3, *E* isomer); 3.79 (s, OCH_3, *Z* isomer)); 7.10—7.30 (m, Ph). ^{13}C NMR, δ: 14.45 (C(1), *E* isomer); 20.97 (C(1), *Z* isomer); 29.88 (C(3), *Z* isomer); 34.13 ($\underline{C}H_2$Ph, $J_{C,P}$ = 60.6 Hz); 34.90 ($\underline{C}H_2$Ph, $J_{C,P}$ = 60.5 Hz); 35.48 (C(3), *E* isomer); 42.11 (C(4), *Z* isomer), $J_{C,P}$ = 60.3 Hz), 42.56 (C(4), *E* isomer, $J_{C,P}$ = 60.6 Hz), 60.99 (OCH_3, *Z* isomer); 61.04 (OCH_3, *E* isomer); 126.93 (C_p); 127.24 (C(8)); 128.34 (C(7)); 128.58 (C_m); 129.47 (C(6), $J_{C,P}$ = 5.5 Hz); 129.86 (C_o, $J_{C,P}$ = 5.6 Hz); 132.04 (C_{ipso}, *Z* isomer, $J_{C,P}$ = 6.7 Hz); 132.08 (C_{ipso}, *E* isomer, $J_{C,P}$ = 6.5 Hz); 135.98 (C(5), *Z* isomer, $J_{C,P}$ = 5.3 Hz); 136.54 (C(5), *E* isomer, $J_{C,P}$ = 4.8 Hz); 153.67 (C(3), *E* isomer, $J_{C,P}$ = 12.6 Hz); 155.29 (C(3), *Z* isomer, $J_{C,P}$ = 12.2 Hz).

3-Amino-5-benzyl-9,9-dimethyl-5-oxo-4-phenyl-5-phosphatricyclo[6.1.1.0^{2,5}]dec-3-ene (13) was isolated as a light crystalline substance using column chromatography of the product prepared from myrtenal *O*-methyloxime **9** (0.60 g, 3.4 mmol). The yield was 0.30 g (24%). The substance was identical to the sample obtained previously from myrtenonitrile.[4]

3-Dibenzylphosphinoyl-10-nor-α-pinene (14) was isolated by column chromatography on silica gel of the product prepared from myrtenal *O*-methyloxime **9** (0.60 g, 3.4 mmol). The yield was 0.30 g (26%). Yellowish crystals with m.p. 127—130 °C (from Bu^tOMe), $[\alpha]^{24}_{578}$ −53.6 (*c* 2.09). MS, *m/z* (I_{rel}(%)): 350.18173 (59%, calculated for $C_{23}H_{27}OP$ 350.17995), 309 (18), 307 (13), 259 (14), 139 (24), 120 (10), 91 (100). IR (*c* = 2%, $CHCl_3$), ν/cm^{-1}: 3090, 1600, 1495, 1455, 1190, 825. ^{31}P NMR, δ: 32.98. ^{1}H NMR, δ: 0.49 (s, 3 H, H(8)); 0.84 (d, 1 H, H(7α), *J* = 8.3 Hz); 1.18 (s, 3 H, H(9)); 2.09 (m, 1 H, H(5)); 2.20 (m, 4 H, H(1), H(4) and H(7β)); 2.88—3.29 (m, 4 H, C$\underline{H}_2$Ph); 6.98 (dd, H(2), *J* = 16.0, 6.3 Hz); 7.14—7.34 (m, 10 H, Ph). ^{13}C NMR, δ: 20.90 (C(8)); 25.86 (C(9)); 30.65 (C(7), $J_{C,P}$ = 3.2 Hz); 31.22 ($\underline{C}H_2$Ph, $J_{C,P}$ = 63.8 Hz); 31.27 ($\underline{C}H_2$Ph, $J_{C,P}$ = 63.8 Hz); 31.85 (C(4) $J_{C,P}$ = 8.6 Hz); 38.10 (C(6), $J_{C,P}$ = 2.8 Hz); 40.70 (C(5), $J_{C,P}$ = 8.6 Hz); 42.62 (C(1), $J_{C,P}$ = 12.3 Hz); 126.41 (C(3), $J_{C,P}$ = 93.3 Hz); 126.54 (C_p, $J_{C,P}$ = 2.6 Hz); 126.61 (C_p, $J_{C,P}$ = 2.4 Hz); 128.29 (C_m, $J_{C,P}$ = 2.2 Hz); 128.42 (C_m, $J_{C,P}$ = 2.0 Hz); 129.65 (C_o, $J_{C,P}$ = 5.2 Hz); 129.72 (C_o, $J_{C,P}$ = 5.4 Hz); 131.84 (C_{ipso}, $J_{C,P}$ = 7.3 Hz); 131.92 (C_{ipso}, $J_{C,P}$ = 7.3 Hz), 154.06 (C(2), $J_{C,P}$ = 3.9 Hz).

[1,2-Bis(dibenzylphosphinoyl)ethyl]benzene (15) was isolated as a light crystalline substance by recrystallization from acetonitrile of the product prepared from cinnamal *O*-methyloxime (**10**) (0.37 g, 2.3 mmol). The yield was 0.67 g (52%). The product was identical to the substance obtained from cinnamonitrile.[3]

3-Amino-1-benzyl-5-methyl-5-(4-methylpent-3-enyl)-1-oxo-2-phenyl-4,5-dihydro-1*H*-phosphole (16) was synthesized as a light crystalline substance from citral *O*-methyloxime (**11**) (0.45 g, 2.5 mmol). The yield was 0.47 g (50%). The substance was identical to the product synthesized from geranylnitrile.[3]

3-Amino-1-benzyl-5-ethyl-4-methyl-1-oxo-2-phenyl-4,5-dihydro-1*H*-phosphole (17) was synthesized as a light crystalline substance from 2-methylpent-2-enal *O*-methyloxime (**12**) (0.3 g, 2.4 mmol). The yield was 0.24 g (30%). The substance was identical to the sample synthesized from 2-methylpent-2-enonitrile.[3]

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