Synthesis of chiral organophosphorus compounds by the reaction of dibenzylphosphine oxide with α,β-unsaturated ketones of the terpene series

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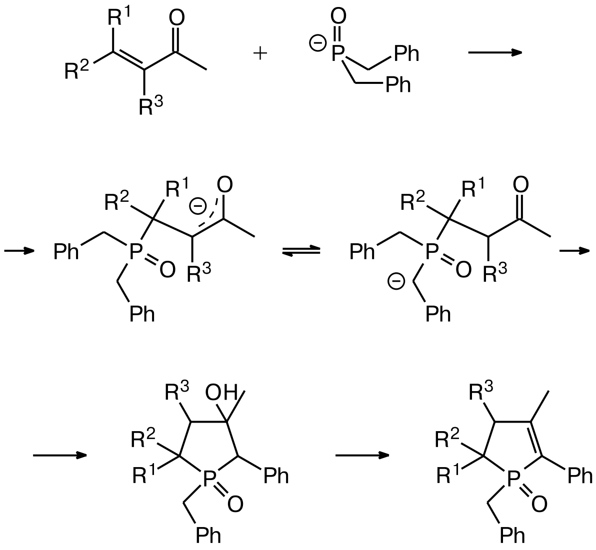
Dibenzylphosphine oxide readily reacts with α,β-unsaturated terpene ketones in aprotic media to form both chiral phosphorus-containing heterocycles and acyclic chiral phosphine oxides.

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

It is known that heterocyclic derivatives of organophosphorus compounds exhibit a wide spectrum of biological activity.[1,2] The addition of trivalent phosphorus halides to dienes[3—5] has remained for a long time to be the main method for the syntheses of five-membered phosphorus-containing heterocycles, but in the 1970s a new method was proposed. The method is based on the reaction of α,β-unsaturated esters[6] or ketones[7] with derivatives of phosphonous and phosphinous acids (secondary phosphine oxides) containing the benzyl radical. Phospholane compounds have previously[7] been synthesized by the reaction of dibenzylphosphine oxide with aliphatic α,β-unsaturated ketones (Scheme 1). However, stereochemical requirements of this reaction were not studied, and the range of substrates was rather limited.

Scheme 1



In the present work, we studied the reactions of dibenzylphosphine oxide with α,β-unsaturated aliphatic and arylalkenyl ketones of the terpene series bearing different combinations of substituents in the α-, β-, and γ-positions and differing in steric hindrance of the carbonyl group. The reactions with aliphatic ketones **1**, **2**, and **3** easily afforded five-membered P-heterocycles (Scheme 2).

The presence of the P-heterocycle in the resulting products is confirmed by spectroscopic methods. The data from the IR and NMR spectra indicate that molecules **4—6** have no carbonyl group but contain the phosphoryl group (a strong broad band at 1150—1250 cm^{-1} in the IR spectra). The ^{13}C NMR spectra exhibit direct spin-spin coupling constants of three carbon atoms on the phosphorus atom, and their values are characteristic of phosphine oxides (50—70 Hz).[8,9] The chemical shifts of the P atoms in the ^{31}P NMR spectra are typical of five-membered P-heterocycles (δ_P = 50—65), while the standard values of chemical shifts for acyclic phosphine oxides are δ_P 40—50.[8] The structures of the obtained organophosphorus compounds were established using two-dimensional NMR spectroscopy.

The reaction of acyclic ketone **1** with dibenzylphosphine oxide affords a mixture of two products (**4a,b**) in the ratio 1 : 1. Both products have the same mass spectra (GLC-MS) and similar ^{13}C NMR spectra. A comparison of the spectra of the products and the initial ketone suggests that the 2,6-dimethylhept-5-enyl radical has retained in the products. According to the NMR spectroscopic data, these products are C(6)-epimers.

The identical chemical shifts of the phosphorus atoms in the ^{31}P NMR spectrum and of the C(5) atom in the ^{13}C

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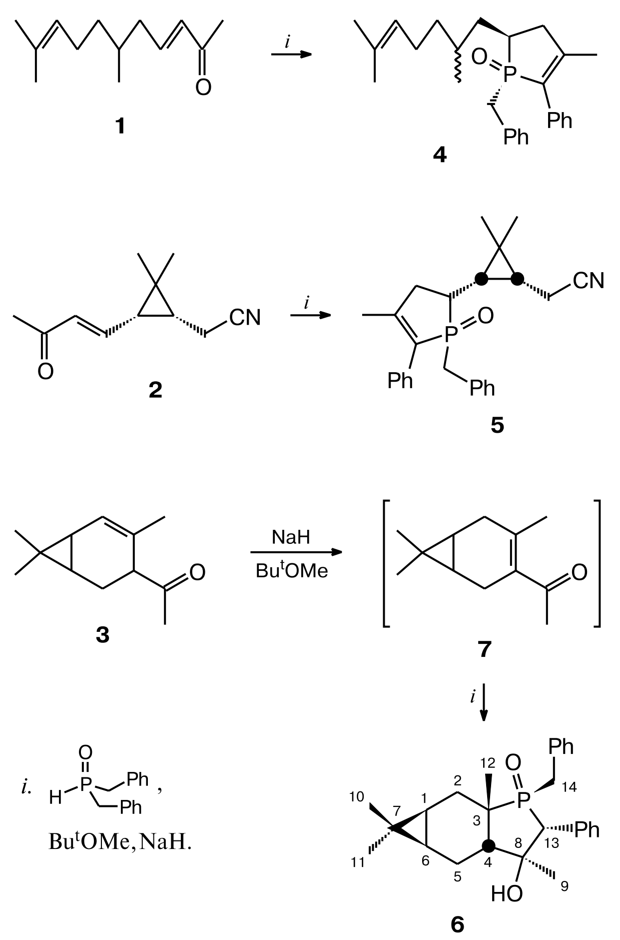
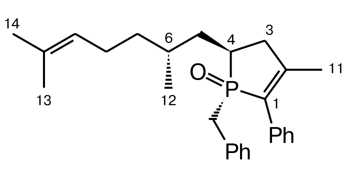
Scheme 2

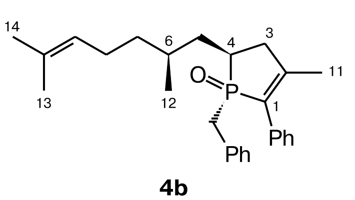


Note. Hereinafter the numeration of atoms is presented for the description of NMR spectra.

NMR spectrum indicate that the configuration of the P-heterocycle is the same in both isomers. The H(4)—P spin-spin coupling constant (J = 5.0 Hz) indicates the transoid arrangement of the H(4) atoms and the phosphoryl oxygen.[9] The greatest differences in the ^{1}H and ^{13}C NMR spectra are observed for the C(12) methyl group (δ_H 0.80 and 0.86, δ_C 18.46 and 19.70) and C(6) atom (δ_C 30.80 and 30.35).



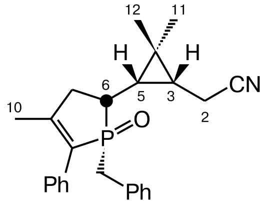
4a



4b

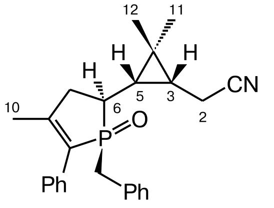
Thus, the phosphorus reagent adds at both sides of the C=C double bond with almost equal rates, while ring closure to form phospholane is highly stereoselective. This suggests that the addition of dibenzylphosphine oxide to the double bond (see Scheme 1) is fast and little sensitive to steric hindrances, whereas ring closure with the formation of phospholane is more exacting to steric interactions and affords a thermodynamically more stable isomer only.

The addition of dibenzylphosphine oxide to cyclopropane-containing ketone **2** also produces a mixture of products but in the ratio 2 : 1. As in the case of dihydrophosphole oxide **4**, these products have identical mass spectra (according to the GLC-MS data) and similar IR and NMR spectra. Analysis of the spectroscopic data suggests that the products are isomers of dihydrophosphole oxide **5**. One of them was isolated by chromatography on Al_2O_3. The H(3)—H(5) spin-spin coupling constant (J = 9.0 Hz) for this isomer and a great difference in chemical shifts of the C(11) and C(12) methyl groups in the ^{13}C NMR spectrum (δ_C 13.50 and 27.97) indicate that the cyclopropane fragment has retained the cisoid configuration. The high spin-spin coupling constant of the H(6) atom and phosphorus atom (J = 22.0 Hz) indicates the cisoid arrangement of this hydrogen atom and the phosphoryl oxygen. Structures **5a** and **5b** satisfy these requirements.



5a

or



5b

Isomers **5a** and **5b** can be formed due to the attack on the carbon—carbon bond in compound **2** by the phosphorus reactant from opposite sides. Available data do not allow the exact assignment to be performed for both the isolated and nonisolated isomers of dihydrophosphole oxide **5**.

4-Acetylcar-2-ene (**3**) does not contain a conjugated system and formally is inappropriate as a substrate for this reaction. However, compound **3** reacts in such a way as if it is a conjugated ketone. Published data indicate a possibility of isomerization of 4-acetylcar-2-ene (**3**) to 4-acetylcar-3-ene (**7**) in the presence of a base.[10] Since dibenzylphosphine oxide reacts with conjugated ketones in the presence of a strong base (sodium hydride), these conditions create a possibility to form reactive conjugated 4-acetylcar-3-ene (**7**) from 4-acetylcar-2-ene (**3**). The further reaction of ketone **7** with dibenzylphosphine oxide affords tricyclic phospholane **6**.

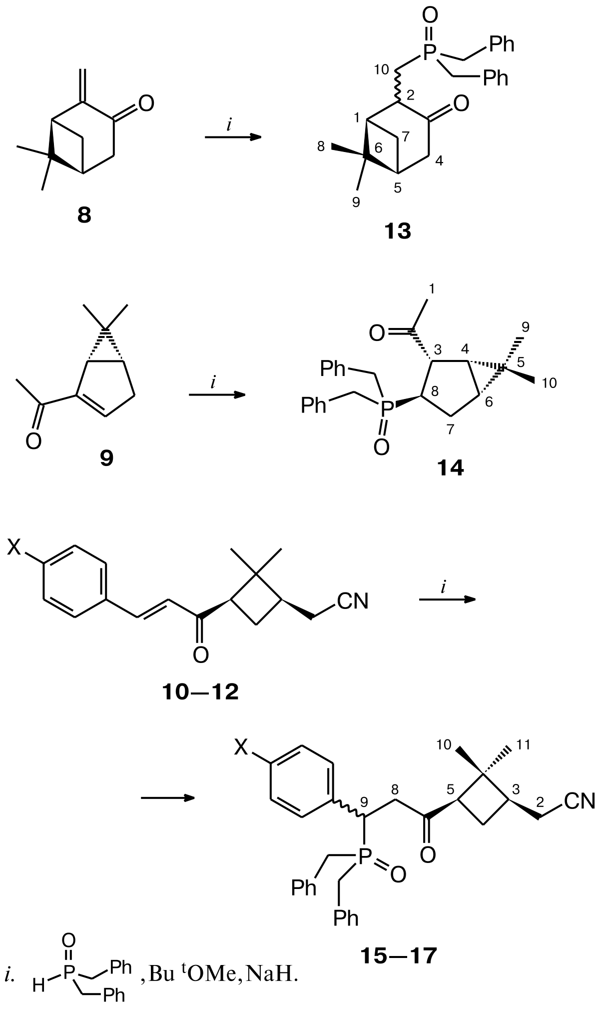
Unlike ketones **1** and **2**, the reaction of acetylcarene **3** with dibenzylphosphine oxide stops at the step of formation of hydroxyphospholane **6**. This is related, most likely, to the configuration of the hydroxy group in the molecule of **6**. Attempts to bring the reaction to the formation of dihydrophosphole oxide by increasing the reaction time or the amount of a base resulted only in the decomposition of hydroxyphospholane **6**.

The presence of the hydroxy group in the molecule is confirmed by the IR spectrum (ν 3600—3300 cm^{-1}). The data from the ^{13}C NMR spectrum indicate that the molecule does not contain olefinic carbon atoms bound to the phosphorus atom. At the same time, the spectrum exhibits a signal for the secondary sp^3-hybridized carbon atom with the direct spin-spin coupling constant on the phosphorus atom (63.6 Hz). The patterns of the aliphatic part in the ^{1}H and ^{13}C NMR spectra are typical of carane compounds, indicating that the carane skeleton (3,7,7-trimethylbicyclo[4.1.0]heptane) has retained in a molecule of compound **6**.

The spatial structure of a molecule of compound **6** was established from the NMR spectroscopic data. One of the sides of the double carbon—carbon bond of conjugated ketone **7** is blocked by the methyl group of the *gem*-dimethyl fragment. Therefore, the phosphorus reactant cannot add from the side of cyclopropane. Thus, the phosphorus atom in phospholane **6** should be in the transoid position relative to the cyclopropane ring. This is confirmed by the fact that the spin-spin coupling constant of the H(2β) atom and phosphorus atom (J = 27.0 Hz) corresponds to the antiperiplanar arrangement of these atoms. The ^{1}H NMR spectrum exhibits sufficiently high and similar H(1)—H(2α) and H(1)—H(2β) spin-spin coupling constants and strong shielding of the H(2β) (δ_H 0.62) and H(5β) (δ_H 0.96) protons. These data show that the six-membered cycle should exist in the boat conformation,[11] which is possible only for *cis*-fusion of the six- and five-membered rings, judging from the conformation analysis data using MM2 calculations. This fusion is confirmed by the homonuclear Overhauser effect: irradiation of protons of the H(12) methyl group enhances the intensity of the signal for the H(4) proton (4%). The spin-spin coupling constant of the H(13) atom on the phosphorus atom is 7.0 Hz, which points to the transoid orientation of this hydrogen atom and the phosphoryl oxygen. In addition, the homonuclear Overhauser effect between the H(12), H(13) atoms and benzyl H(14) protons indicates their cisoid arrangement. Thus, in the molecule of compound **6** the cyclohexane ring has the boat conformation and is *cis*-fused with the phospholane cycle, and the phosphoryl oxygen and phenyl group at the C(13) atom have transoid orientation with respect to the methyl group at C(3).

The configuration of the C(8) atom in compound **6** was determined as follows. For the β-configuration of the C(9)H$_3$ methyl group, the semiempirical quantum-mechanical calculaltions using the PM3 method give the structure whose cyclohexane ring exists in the twist form. For this form, the values of the H(1)—H(2α), H(1)—H(2β), and H(4)—P dihedral angles (96°, 17°, and 79°, respectively) do not correspond to the experimental spin-spin coupling constants (9, 9, and 7 Hz, respectively).[9,11] For the α-configuration of this methyl group, the calculations give a confirmation with the cyclohexane ring in the boat-like form. In this case, the experimental spin-spin coupling constants agree well with both the dihedral angles mentioned (φ(H(1)—H(2α)) = 26°, φ(H(1)—H(2β)) = 141°, φ(H(4)—P) = 111°) and the φ(P—C(9) dihedral angle (φ = 140°, J = 10 Hz).[9,11] In addition, the α-orientation of the C(9)H$_3$ group and β-orientation of the hydroxy group are favorable from the viewpoint of minimization of the dipole-dipole interaction of the hydroxy group with the phosphoryl group, which are transoid in such a configuration. This type of interaction seems to be very critical at the cyclization step.

Scheme 3



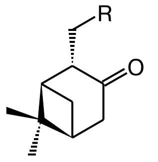
i. H–P(O)(CH$_2$Ph)$_2$, Bu^{t}OMe, NaH.

X = H (**10**, **15**), OMe (**11**, **16**), NMe$_2$ (**12**, **17**)

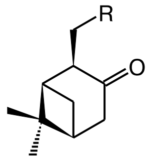
In addition to the above mentioned ketones, we introduced pinocarvone **8**, bicyclic ketone **9**, and fatty aromatic ketones **10**, **11**, and **12** synthesized from α-pinene into reactions with dibenzylphosphine oxide (Scheme 3).

The reaction of dibenzylphosphine oxide with these ketones did not afford P-heterocycles. The IR spectra of the products of these reactions contain absorption bands corresponding to the carbonyl and phosphoryl groups. The chemical shifts of the phosphorus atom in the ^{31}P NMR spectra of the reaction products lie in the region characteristic of acyclic phosphine oxides (δ_P 40—46),[8] which allowed us to conclude that these products are β-phosphoryl ketones (see Scheme 3).

According to the NMR data, β-phosphoryl ketone synthesized from pinocarvone **8** retains the pinane carbon skeleton and represents a mixture (in the ratio of 3 : 1) of isomeric pinocamphone and isopinocamphone derivatives **13**. The configuration of the C(2) atom was determined by a comparison of the ^{13}C NMR spectrum of this compound with the spectra of isopinocamphone oxime[12] and isomeric pinocamphone.[13] For the pinocamphone—isopinocamphone pair, the chemical shifts of the C atoms of the *gem*-dimethyl fragment for pinocamphone are known[13] to be smaller. The chemical shifts of the C(8) and C(9) methyl groups of the major isomer of compound **13** are δ_C 19.47 and 25.98, and those of the minor isomer are δ_C 21.62 and 26.50, respectively. This indicates that the major isomer is a pinocamphone derivative.



Pinocamphone
derivatives



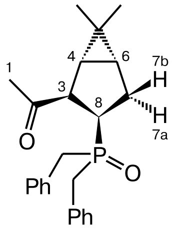
Isopinocamphone
derivatives

R = P(O)(CH$_2$Ph)$_2$

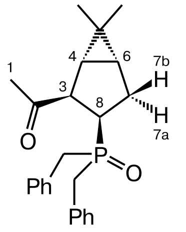
In addition, signals for the C(2) and C(7) carbon atoms should be considered. They can also be used for the determination of the pinane skeleton configuration. It is known that the chemical shifts of these C atoms are in higher fields for pinocamphones than for isopinocamphones.[13] The chemical shifts for C(2) of the major and minor isomers (δ_C 46.00 compared to 49.48) and C(7) (δ_C 28.67 compared to 34.10) also indicate the pinocamphone configuration of the major isomer.

β-Phosphoryl ketone synthesized from bicyclic ketone **9** also retained the carbon skeleton of the initial ketone. Based on the spectroscopic data, we ascribed the structure of **14** to this ketone (see Scheme 3). Unlike pinocamphone derivative **13**, compound **14** was obtained as a single isomer. Its configuration was established from the spectroscopic data and calculations.

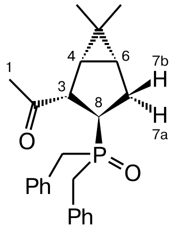
Molecular simulation shows that one of the sides of the carbon—carbon double bond of ketone **9** is almost completely blocked by one of the *gem*-dimethyl groups. Therefore, the bulky phosphorus reactant can add only to the side opposite to the *gem*-dimethyl fragment. Thus, the phosphoryl group in compound **14** should be transoid with respect to the cyclopropane fragment. The configuration of the acetyl residue was determined from the spin-spin coupling constants. The calculations show that the five-membered cycle can exist in two conformations: (1) all atoms of the cycle are virtually coplanar and (2) the C(8) atoms deviate from the plane to the side opposite to cyclopropane. As a result, four stereoisomers presented in Fig. 2 are possible.



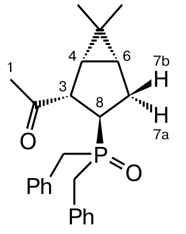
14A



14B



14C



14D

The geometric parameters for four possible isomers of compound **14** calculated by the PM3 method and experimental spin-spin coupling constants are presented in Table 1. Isomers **14C** and **14D** demonstrate the best fit of these parameters with experimental data. The difference from experimental data can be caused by both inadequacy of parametrization of empirical formulas for the calculation of the spin-spin coupling constants and interconversions of conformers **14C** and **14D**. Evidently, the barrier for this conversion should be of an order of magnitude of the barrier for cyclopentane pseudorotation. Thus, we can believe that the exchange spectrum with averaged spin-spin coupling constants is really observed.

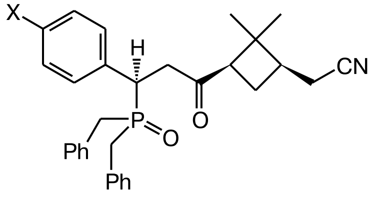
β-Phosphoryl ketones **15**, **16**, and **17** synthesized from the corresponding cyclobutyl styryl ketones (see Scheme 3) were isolated as mixtures of stereoisomers.

β-Phosphoryl ketone **15** is formed as a pair of stereoisomers **15A** and **15B** in the ratio 3 : 2. Analysis of the NMR spectra indicates that these compounds retain the *cis*-disubstituted cyclobutane fragment and are epimers at the C(9) atom. This conclusion is favored by a slight

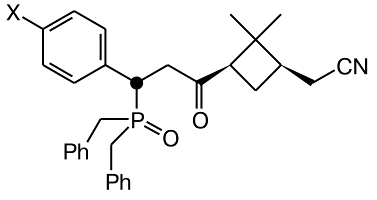
Table 1. Calculated heats of formation (ΔH_f/kcal mol^{-1}), geometrical parameters (φ/deg), and spin-spin coupling constants[9,11,14] (J/Hz) for the isomers of β-phosphoryl ketone **14**

Parameter	Experiment	Calculation (PM3)			
		14A	**14B**	**14C**	**14D**
ΔH_f		−33.29	−30.71	−29.9	−35.94
$J_{H(3)-H(4)}$	6.8	~3	~2	~4	~7
φ(H(3)—H(4))		110	90	119	37
$J_{H(3)-H(8)}$	8.1	~11	~10	~9	~9
φ(H(3)—H(8))		10	21	24	143
$J_{H(3)-P}$	19.7	~16	~0	~25.5	~15.5
φ(H(3)—P)		129	95	142	22
$J_{H(7a)-H(8)}$	10.0	~11	~9	~10	~10
φ(H(7a)—H(8))		1	29	15	18
$J_{H(7b)-H(8)}$	8.7	~4.5	~10	~3	~8
φ(H(7b)—H(8))		117	147	103	136
$J_{H(7a)-H(6)}$	0	~2.5	~2.5	~3	~2
φ(H(7a)—H(6))		97	84	109	89
$J_{H(7b)-H(6)}$	6.7	~9.5	~8	~10	~8
φ(H(7b)—H(6))		18	32	8	29
$J_{H(7a)-P}$	6.1	~4	~0	~15	~1.5
φ(H(7a)—P)		109	84	127	101
$J_{H(7b)-P}$	20.6	~18	~12	~17.5	~16
φ(H(7b)—P)		7	36	9	18

difference in chemical shifts in the ^{13}C NMR spectra for the carbon atoms of the acetonitrile and cyclobutane fragments. Compounds **16** and **17** are also formed as pairs of stereoisomers.



A



B

X = H (**15**), OMe (**16**), NMe_2 (**17**)

As should be expected, the rate of dibenzylphosphine oxide addition to conjugated ketones **11** and **12** has decreased noticeably compared to the reaction of ketone **10** because the electron-donating substituents in the aromatic cycle decreased the electrophilicity of the carbon—carbon double bond.

An interesting fact should necessarily be noted: the $C(10)H_3$ group in these compounds in the ^{1}H NMR spectra is unusually strongly shielded (δ_H 0.25—0.31). The PM3 calculations show that for the *cis*-configuration of the cyclobutane ring the phenyl group is approached to the $C(10)H_3$ methyl group in such a way that it is localized directly above the benzene ring plane, which results in its shielding due to the anisotropic influence of the aromatic fragment.

As in the case of β-phosphoryl ketones **13** and **14**, attempts to obtain cyclic products from compounds **15—17** were unsuccessful: an increase in the temperature or duration of the reaction resulted in resinification only. It remains unclear why dihydrophosphole oxides cannot be obtained from ketones **8—12**. No regularities were revealed to explain the reactivity of β-phosphoryl ketones: the PM3 calculation of the activation energy of their ring closure to hydroxyphospholane oxides did not reveal a correlation between the activation energy and the formation of five-membered P-heterocycles. It is most likely that some special factors inherent in the given structure are important in each particular case. As can be seen in Scheme 1, the enolate anion should be transformed into the benzyl anion for ring closure to occur. According to PM3 calculations, the stability of the benzyl anion slightly exceeds the stability of the enolate anion. In the case where such an order of stability is violated for some reasons, ring closure should substantially be impeded.

The ratio of isomers of β-phosphoryl ketone **13** is close to the thermodynamically equilibrium ratio. Based on this fact, we can conclude that this compound exists in the reaction medium as the enolate anion. The formation of this enolate anion is favorable because the appearance of two sp^2-hybridized carbon atoms, *viz*., C(2) and C(3), decreases the steric strain in the pinane skeleton.

β-Phosphoryl ketone **14** was isolated as the single isomer but in this case ring closure to phospholane is prevented by the transoid orientation of the phosphoryl and carbonyl groups.

In the case of compounds **15—17**, the semiempirical quantum-chemical PM3 calculations show that the most acidic protons in β-phosphoryl ketones **15**, **16**, and **17** are in the C(9) and C(8) positions. Thus, the benzyl anion necessary for ring closure (see Scheme 1) is not formed, and the reaction stops at the step of β-phosphoryl ketone.

Thus, this study shows that terpene unsaturated ketones readily react with dibenzylphosphine oxide under aprotic conditions to form, depending on the substrate structure, both phosphorus-containing heterocycles and acyclic phosphine oxides. Analysis of the spatial structure of the obtained products suggests that the addition of a phosphorus reactant to the olefinic bond of α,β-unsaturated ketone is fast and little sensitive to steric hindrances. At the same time, the ring closure to phospholane is the rate-limiting step of the reaction and depends strongly on the spatial environment of the reaction center.

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 concentrated H_2SO_4 in 150 mL of EtOH) or iron chloride (10% $FeCl_3 \cdot 6H_2O$ in 150 mL of EtOH) and heated. For preparative column chromatography, Al_2O_3 (Russia, TU 6-09-3916-75, activated at 250 °C for 3 h) was used. 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 (^{1}H, 500.13 MHz; ^{13}C, 125.75 MHz) for solutions with concentrations of 70—100 mg mL^{-1} at 25—27 °C. Signals from residual protons of the deuterated solvent (chloroform-d, δ_C 76.90, δ_H 7.24) were used as internal standards. ^{31}P NMR were recorded under the same conditions on a Bruker AC-200 instrument (^{31}P, 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 of atoms with even and odd numbers of added protons tuned to the constant J = 135 Hz) and from the data of two-dimensional spectra: (1) homonuclear ^{1}H—^{1}H correlation, (2) heteronuclear ^{13}C—^{1}H correlation on direct spin-spin coupling constants (J = 135 Hz), (3) heteronuclear ^{13}C—^{1}H correlation on long-range spin-spin coupling constants (J = 10 Hz), and (4) ^{1}H *J*-resolved spectra. Optical rotation was determined on a Polamat A polarimeter for solutions in $CHCl_3$. Melting points were determined on a Koffler stage.

(−)-Pinocarvone **8** was synthesized by the photooxidation of (−)-α-pinene.[15] Ketones **1** and **2** were synthesized from (±)-citronellal and (2,2-dimethyl-3-formylcyclopropyl)acetonitrile[16] using the Wittig reaction.[17] Acetylcarene **3** [10] and bicyclic ketone **9** [18] were synthesized from (+)-3-carene using known procedures. Aryl ketones **10**, **11**, and **12** (racemic mixtures) were kindly presented by A. M. Chibiryaev (Novosibirsk Institute of Organic Chemistry, Siberian Branch of the RAS). Dibenzylphosphine oxide was synthesized by the reaction of diethyl phosphite with benzylmagnesium chloride.[19]

Reaction of dibenzylphosphine oxide with unsaturated terpene ketones (general procedure). To a solution of dibenzylphosphine oxide (1.56 g, 6.80 mmol) in Bu^{t}OMe (25 mL), 60% NaH (0.54 g, 13.60 mmol) was added. The solution was refluxed with stirring until evolution of hydrogen ceased. Then a solution of an unsaturated ketone (6.80 mmol) in Bu^{t}OMe (10 mL) was added dropwise to the reaction mixture. The resulting mixture was refluxed with stirring until the initial ketone disappeared (TLC). The reaction mixture was cooled to ~20 °C, diluted with Bu^{t}OMe (10 mL), and washed with a saturated solution of NaCl (30 mL). The organic extract was dried with Na_2SO_4, and the solvent was evaporated *in vacuo*. The residue was dried *in vacuo* using an oil pump. The products were purified by passing through Al_2O_3 and recrystallization.

(1*S,2*S**)-1-Benzyl-2-((2*RS*)-2,6-dimethylhept-5-enyl)-4-methyl-5-phenyl-2,3-dihydrophosphole 1-oxide (4) (a mixture of epimers, 1 : 1)** was synthesized from 6,10-dimethylundeca-3,9-dien-2-one (**1**) (0.40 g, 2.1 mmol) as a viscous light yellow oil. The duration of the reaction was 2 h. The yield after passing through a layer of Al_2O_3 was 0.59 g (70%). High-resolution mass spectrum. Found: *m/z* 406.24333. $C_{27}H_{35}OP$. Calculated: M = 406.24254. MS, *m/z* (I_{rel} (%)): 406 (100), 337 (32), 324 (22), 315 (20), 296 (21), 295 (81), 283 (16), 282 (76), 281 (23), 254 (17), 191 (31), 143 (10), 129 (12), 115 (11), 91 (44), 69 (13), 41 (26). IR (*c* 2%, $CHCl_3$), ν/cm^{-1}: 3050, 1500, 1450, 1380, 1200.

NMR spectra (hereinafter 5 mg). ^{31}P NMR, δ: 68.20. ^{1}H NMR, δ: 0.80, 0.86 (both d, 3 H each, H(12), J = 6.4 Hz, J = 7.4 Hz); 1.00, 1.34 (both md, 1 H each, H(5a), J = 14.0 Hz); 1.15—1.28 (m, 4 H, H(7)); 1.33, 1.66 (both mdd, 1 H each, H(5b), J = 14.0 Hz, J_{H-P} = 14.0 Hz); 1.43, 1.44 (both m, 1 H each, H(6)); 1.57, 1.60 (both s, 3 H each, H(13)); 1.65, 1.68 (both s, 3 H each, H(14)); 1.824, 1.828 (both s, 3 H each, H(11)); 1.93, 1.95 (both m, 2 H each, H(8)); 2.08, 2.21 (both md, 1 H each, H(4), J_{H-P} = 5.0 Hz); 2.26, 2.30 (both mdd, 1 H each, H(3a), J = 19.0 Hz, J_{H-P} = 3.0 Hz); 2.39, 2.45 (both mdd, 1 H each, H(3b), J = 19.0 Hz, J_{H-P} = 20.0 Hz); 3.07—3.26 (m, 8 H, CH_2Ph); 5.05, 5.07 (both tq, 1 H each, H(9), J = 7.0 Hz, J = 1.4 Hz); 7.00—7.45 (m, 20 H, Ph). ^{13}C NMR, δ: 17.35 (C(13)); 17.65, 17.76 (C(11), J_{C-P} = 5.7 Hz); 18.46, 19.70 (C(12)); 24.88, 25.07 (C(8)); 25.35 (C(14)); 28.81, 28.91 (C(4), J_{C-P} = 69.2 Hz); 30.35, 30.80 (C(6), J_{C-P} = 8.8 Hz, J_{C-P} = 11.3 Hz); 35.52 (C(5), J_{C-P} = 16.0 Hz); 37.16 (C(7)); 37.38, 37.48 (CH_2Ph, J_{C-P} = 60.0 Hz); 40.66, 41.34 (C(3), J_{C-P} = 9.0 Hz, J_{C-P} = 9.1 Hz); 124.22, 124.36 (C(9)); 126.23, 126.93 (C_p); 128.11, 128.20 (C_m); 128.27, 129.14 (C_o, J_{C-P} = 4.1 Hz, J_{C-P} = 4.5 Hz); 130.75 (C(10)); 132.05, 133.76 (C_{ipso}, J_{C-P} = 6.5 Hz, J_{C-P} = 11.2 Hz); 154.47, 154.71 (C(2), J_{C-P} = 2.3 Hz, J_{C-P} = 4.5 Hz).

[(1*R*,3*S*)-3-(1-Benzyl-4-methyl-1-oxo-5-phenyl-2,3-dihydro-1*H*-1λ^5-phosphol-2-yl)-2,2-dimethylcyclopropyl]acetonitrile (5) was synthesized from ketone **2** (0.27 g, 1.5 mmol) as a viscous light yellow oil. The duration of the reaction was 2 h. The yield of a mixture of epimers (2 : 1) after passing through a layer of Al_2O_3 was 0.55 g (92%), $[\alpha]_{580}^{26}$ = +75.74 (*c* 3.25). The fraction enriched in one of the isomers (7 : 2, $[\alpha]_{580}^{26}$ = +1.34 (*c* 8.93)) was obtained by chromatography on Al_2O_3. High-resolution mass spectrum. Found: *m/z* 389.19038. $C_{25}H_{38}NOP$. M = 389.19084. MS, *m/z* (I_{rel} (%)): 389 (94), 374 (10), 350 (21), 349 (89), 299 (14), 298 (60), 283 (23), 282 (100), 281 (52), 258 (15), 254 (35), 246 (11), 205 (10), 192 (11), 190 (63), 143 (12), 129 (17), 128 (14), 115 (22), 109 (32), 91 (76), 65 (12). IR (*c* 3%, $CHCl_3$), ν/cm^{-1}: 3100—2800 (C—H); 2250 (CN); 1490, 1210 (P=O); 1010.

NMR spectra. ^{31}P NMR, δ: 66.77 (minor isomer); 65.45 (major isomer). ^{1}H NMR (major isomer), δ: 0.51 (ddd, 1 H, H(3), J_1 = 11.0 Hz, J_2 = 9.0 Hz, J_3 = 4.5 Hz); 0.58 (ddd, 1 H, H(5), J_1 = 12.0 Hz, J_2 = 9.0 Hz, J_{H-P} = 4.0 Hz); 0.97 (s, 3 H, H(11)); 1.02 (s, 3 H, H(12)); 1.80 (s, 3 H, H(10)); 1.90 (dddd, 1 H, H(6), J_1 = 12.0 Hz, J_2 = J_3 = 8.2 Hz, J_{H-P} = 22.0 Hz); 1.97 (dd, 1 H, H(2a), J_1 = 18.0 Hz, J_2 = 11.0 Hz); 2.10 (m, 1 H, H(7a)); 2.37 (dd, 1 H, H(2b), J_1 = 18.0 Hz, J_2 = 4.5 Hz); 2.64 (ddd, 1 H, H(7b), J_1 = 17.5 Hz, J_2 = 9.0 Hz, J_{H-P} = 22.0 Hz); 3.01 (dd, 1 H, H(13a), J = 15.0 Hz, J_{H-P} = 12.2 Hz); 3.15 (dd, 1 H, H(13b), J = 15.0 Hz, J_{H-P} = 15.0 Hz); 7.03—7.40 (m, 10 H, Ph). ^{31}C NMR (major isomer), δ: 13.50 (C(11)); 13.68 (C(2)); 17.92 (C(10), J_{C-P} = 12.7 Hz); 18.85 (C(4), J_{C-P} =

11.8 Hz); 23.20 (C(3)); 25.98 (C(5)); 27.97 (C(12)); 34.50 (C(13), J_{C-P} = 58.1 Hz); 36.32 (C(6), J_{C-P} = 65.4 Hz); 39.42 (C(7), J_{C-P} = 14.0 Hz); 119.12 (C(1)); 126.23 (C_p); 127.00 (C_p); 127.68 (C_m); 127.90 (C_m); 128.44 (C_o, J_{C-P} = 3.9 Hz); 129.46 (C_o, J_{C-P} = 5.3 Hz); 131.16 (C_{ipso}, J_{C-P} = 6.9 Hz); 131.37 (C(9), J_{C-P} = 90.8 Hz); 132.95 (C_{ipso}, J_{C-P} = 9.3 Hz); 152.55 (C(8), J_{C-P} = 27.9 Hz).

(1a*R*,2a*S*,5a*S*,6a*S*)-5-Benzyl-1,1,3,5a-tetramethyl-5-oxo-4-phenyldecahydro-5λ^5-phosphacyclopropa[*f*]inden-3-ol (6) was synthesized using a standard procedure from 3-acetylcar-2-ene **3** (0.50 g, 2.8 mmol) as white crystals. The duration of the reaction was 5 min (until the starting material disappeared). The yield was 88% (1.01 g). The analytical sample was prepared by recrystallization from CCl_4, m.p. 230—234 °C, $[\alpha]_{580}^{26}$ = –48.2 (*c* 1.12). High-resolution mass spectrum. Found: *m/z* 408.22272. $C_{26}H_{33}O_2P$. Calculated: M = 408.22180. MS, *m/z* (I_{rel} (%)): 408 (96), 390 (12), 365 (100), 339 (21), 320 (92), 319 (35), 310 (12), 309 (38), 396 (17), 395 (15), 273 (25), 272 (15), 271 (24), 270 (12), 231 (39), 230 (22), 229 (19), 211 (13), 139 (21), 135 (14), 91 (91), 43 (13). IR (*c* 3%, $CHCl_3$), ν/cm^{-1}: 3600—3300 (OH); 3100—2870 (C—H); 1595, 1490, 1445, 1130 (P=O).

NMR spectra. ^{31}P NMR, δ: 68.86. ^{1}H NMR, δ: 0.62 (ddd, 1 H, H(2β), J_1 = 15.0 Hz, J_2 = 9.0 Hz, J_{H-P} = 27.0 Hz); 0.89 (s, 3 H, H(10)); 0.94 (m, 1 H, H(6)); 0.96 (mdd, 1 H, H(5β), J_1 = 9.0 Hz, J_2 = 3.0 Hz); 0.98 (s, 3 H, H(11)); 1.04 (ddd, 1 H, H(1), J_1 = J_2 = J_3 = 9.0 Hz); 1.12 (s, 3 H, H(9)); 1.14 (d, 3 H, H(12), J_{H-P} = 15.5 Hz); 1.67 (ddd, 1 H, H(4), J_1 = 6.1 Hz, J_2 = 1.6 Hz, J_{H-P} = 7.3 Hz); 2.07 (ddd, 1 H, H(2α), J_1 = 15.0 Hz, J_2 = 8.5 Hz, J_{H-P} = 13.0 Hz); 2.17 (m, 1 H, H(5α)); 2.66 (d, 1 H, H(13), J_{H-P} = 7.0 Hz); 3.04 (dd, 1 H, H(14a), *J* = 15.0 Hz, J_{H-P} = 11.0 Hz); 3.13 (dd, 1 H, H(14b), *J* = 15.0 Hz, J_{H-P} = 15.0 Hz); 7.08—7.23 (m, 8 H, Ph); 7.44 (m, 2 H, Ph). ^{13}C NMR, δ: 13.91 (C(10)); 17.08 (C(5), J_{C-P} = 2.8 Hz); 18.05 (C(7)); 19.66 (C(6)); 20.20 (C(1)); 25.62 (C(9), J_{C-P} = 10.2 Hz); 27.17 (C(2), J_{C-P} = 2.0 Hz); 28.07 (C(11)); 28.79 (C(12), J_{C-P} = 4.0 Hz); 32.48 (C(14), J_{C-P} = 51.8 Hz); 37.76 (C(3), J_{C-P} = 64.4 Hz); 52.39 (C(13), J_{C-P} = 63.6 Hz); 55.70 (C(4), J_{C-P} = 6.4 Hz); 81.36 (C(8), J_{C-P} = 7.7 Hz); 126.50 (C_p, J_{C-P} = 2.2 Hz); 126.74 (C_p); 127.81 (C_m); 128.05 (C_m, J_{C-P} = 2.1 Hz); 129.69 (C_o, J_{C-P} = 5.1 Hz); 130.29 (C_{ipso}, J_{C-P} = 7.8 Hz); 130.51 (C_o, J_{C-P} = 6.0 Hz); 132.93 (C_{ipso}, J_{C-P} = 4.0 Hz).

(1*R*,2*RS*,5*S*)-2-Dibenzylphosphinoylmethyl-6,6-dimethylbicyclo[3.1.1]heptan-3-one (13) (a mixture of epimers, 3 : 1) was synthesized from pinocarvone **8** (0.50 g, 3.33 mmol) as a white fine crystalline product. The duration of the reaction was 1 h. The yield was 1.05 g (83%), m.p. 112—118 °C (from a mixture hexane—ethyl acetate), $[\alpha]_{578}^{24}$ = –6.4 (*c* 2.5). High-resolution mass spectrum. Found: *m/z* 380.19093. $C_{24}H_{29}O_2P$. Calculated: M = 380.19052. MS, *m/z* (I_{rel} (%)): 380 (15), 311 (10), 289 (64), 244 (12), 230 (20), 139 (41), 133 (21), 93 (11), 91 (100). IR (*c* 0.67%, KBr), ν/cm^{-1}: 3100—2880, 1715, 1495, 1236, 1180, 1130, 850, 765, 700.

NMR spectra. *Major isomer.* ^{31}P NMR, δ: 42.03. ^{1}H NMR, δ: 0.71 (s, 3 H, H(8)); 0.89 (d, 1 H, H(7α), *J* = 11.0 Hz); 1.21 (s, 3 H, H(9)); 1.52 (ddd, 1 H, H(10a), J_1 = 10.2 Hz, J_2 = 13.4 Hz, J_3 = 15.2 Hz); 2.00 (m, 1 H, H(5)); 2.11 (ddd, 1 H, H(10b), J_1 = 3.0 Hz, J_2 = 6.7 Hz, J_3 = 15.2 Hz); 2.15 (m, 1 H, H(1)); 2.29 (m, 1 H, H(7β)); 2.33 (dddd, 1 H, H(4β), J_1 = 19.0 Hz, J_2 = 3.7 Hz, J_3 = 2.3 Hz, J_4 = 1.0 Hz); 2.56 (dd, 1 H, H(4α), J_1 = 3.4 Hz, J_2 = 18.9 Hz); 2.68 (ddm, 1 H, H(2), J_1 = J_2 = 12 Hz); 2.90 (m, 1 H, $C\underline{H}_2Ph$); 3.05 (m, 1 H, $C\underline{H}_2Ph$); 3.18 (m, 2 H, $C\underline{H}_2Ph$); 7.32—7.15 (m, 10 H, Ph). ^{13}C NMR, δ: 19.47 (C(8)); 25.98 (C(9)); 26.97 (C(10), J_{C-P} = 67.2 Hz); 28.67 (C(7)); 36.65 ($\underline{C}H_2Ph$, J_{C-P} = 61.2 Hz); 37.49 ($\underline{C}H_2Ph$, J_{C-P} = 62.1 Hz); 37.66 (C(5)); 39.93 (C(6)); 42.59 (C(1), J_{C-P} = 1.7 Hz); 44.02 (C(4)); 46.00 (C(2), J_{C-P} = 3.4 Hz); 126.76 (C_p); 128.57 (C_m); 129.59 (C_o, J_{C-P} = 5.0 Hz); 129.72 (C_o, J_{C-P} = 5.2 Hz); 131.55 (C_{ipso}, J_{C-P} = 7.1 Hz); 131.93 (C_{ipso}, J_{C-P} = 7.1 Hz); 212.52 (C(3), J_{C-P} = 11.0 Hz). *Data for the minor isomer accessible from the spectra of a mixture of isomers (3 : 1).* ^{31}P NMR, δ: 42.60. ^{1}H NMR, δ: 0.63 (s, H(8)); 1.09 (d, H(7α), *J* = 10.5 Hz); 1.15 (s, H(9)); 1.44 (m, H(10a)). ^{13}C NMR, δ: 21.62 (C(8)); 26.50 (C(9)); 28.13 (C(10)); 34.10 (C(7)); 38.42 (C(5)); 43.86 (C(1), J_{C-P} = 2.2 Hz); 44.41 (C(4)); 49.48 (C(2), J_{C-P} = 3.4 Hz); 212.29 (C(3), J_{C-P} = 9.3 Hz).

(1*R*,2*S*,3*R*,5*R*)-2-Acetyl-3-dibenzylphosphinoyl-6,6-dimethylbicyclo[3.1.0]hexane (14) was synthesized from ketone **9** (0.30 g, 2.00 mmol) as a white fine crystalline product. The duration of the reaction was 1.5 h. The yield was 63% (0.48 g), m.p. 112—114 °C (from Bu^{t}OMe). $[\alpha]_{578}^{24}$ = +15.45 (*c* 0.9). High-resolution mass spectrum. Found: *m/z* 380.19093. $C_{24}H_{29}O_2P$. Calculated: M = 380.19052. MS, *m/z* (I_{rel} (%)): 380 (20), 337 (20), 231 (23), 151 (17), 139 (40), 230 (20), 107 (32), 91 (100), 73 (35), 65 (11), 57 (15). IR (*c* 2%, $CHCl_3$), ν/cm^{-1}: 3100—2880, 1709, 1496, 1454, 1227, 1200, 1152.

NMR spectra. ^{31}P NMR, δ: 45.59. ^{1}H NMR, δ: 0.80 (s, 3 H, H(9)); 0.92 (s, 3 H, H(10)); 1.20 (dd, 1 H, H(6), J_1 = J_2 = 6.9 Hz); 1.48 (dd, 1 H, H(4), J_1 = J_2 = 7.0 Hz); 1.54 (ddd, 1 H, H(7a), J_{H-P} = 6.1 Hz, J_1 = 14.0 Hz, J_2 = 10.0 Hz); 2.07 (s, 3 H, H(1)); 2.26 (dddd, 1 H, H(7b), J_{H-P} = 20.6 Hz, J_1 = 14.0 Hz, J_2 = 8.7 Hz, J_3 = 6.7 Hz); 2.61 (dddd, 1 H, H(8), J_{H-P} = 4.1 Hz, J_1 = 9.7 Hz, J_2 = J_3 = 8.4 Hz); 2.75—3.00 (m, 4 H, $C\underline{H}_2Ph$); 3.37 (ddd, 1 H, H(3), J_{H-P} = 19.7 Hz, J_1 = 8.4 Hz, J_2 = 6.8 Hz); 7.12—7.30 (m, 10 H, Ph). ^{13}C NMR, δ: 15.08 (C(9)); 20.20 (C(5)); 26.06 (C(7), J_{C-P} = 2.2 Hz); 27.76 (C(10)); 28.39 (C(1)); 30.83 (C(6), J_{C-P} = 7.2 Hz); 33.63 (C(4), J_{C-P} = 8.2 Hz); 34.85 ($\underline{C}H_2Ph$, J_{C-P} = 60.0 Hz); 36.08 ($\underline{C}H_2Ph$, J_{C-P} = 60.7 Hz); 38.90 (C(8), J_{C-P} = 63.3 Hz); 53.82 (C(3), J_{C-P} = 2.2 Hz); 126.47 (C_p, J_{C-P} = 2.2 Hz); 126.65 (C_p, J_{C-P} = 2.6 Hz); 128.28 (C_m, J_{C-P} = 1.9 Hz); 128.44 (C_m, J_{C-P} = 2.4 Hz); 129.56 (C_o, J_{C-P} = 4.8 Hz); 129.98 (C_o, J_{C-P} = 5.5 Hz); 132.07 (C_{ipso}, J_{C-P} = 6.5 Hz); 132.12 (C_{ipso}, J_{C-P} = 6.5 Hz); 206.93 (C(2), J_{C-P} = 2.6 Hz).

(1*R,3*R**)-3-[(3*RS*)-3-Dibenzylphosphinoyl-3-phenylpropionyl]-2,2-dimethylcyclobutylacetonitrile (15) (a mixture of epimers, 3 : 2)** was synthesized from unsaturated ketone **10** (0.30 g, 1.18 mmol) as a white crystalline product. The duration of the reaction was 30 min. The yield was 96% (0.55 g), m.p. 149—153 °C (from CCl_4). High-resolution mass spectrum. Found: *m/z* 483.23453. $C_{31}H_{34}O_2PN$. Calculated: M = 483.23270. MS, *m/z* (I_{rel} (%)): 483 (11), 391 (65), 333 (10), 297 (72), 247 (15), 230 (13), 159 (12), 143 (10), 141 (18), 139 (22), 131 (19), 91 (100), 55 (51). IR (*c* 0.25%, KBr), ν/cm^{-1}: 3100—2800 (C—H); 2250 (CN); 1690 (C=O); 1590, 1490, 1440, 1150 (P=O); 820, 750, 690.

NMR spectra. *Major isomer.* ^{31}P NMR, δ: 44.98. ^{1}H NMR, δ: 0.25 (s, 3 H, H(10)); 1.15 (s, 3 H, H(11)); 1.86 (m, 2 H, H(6)); 2.11 (m, 2 H, H(2)); 2.13 (m, 1 H, H(3)); 2.62 (dd, 1 H, H(5), J_1 = 9.5 Hz, J_2 = 7.5 Hz); 2.69 (dd, 1 H, H(8a), J_1 = 15.0 Hz, J_2 = 10.0 Hz); 2.79 (m, 1 H, H(8b)); 2.97 (dd, 2 H, $C\underline{H}_2Ph$, J_1 = 15.0 Hz, J_2 = 11.5 Hz); 3.07 (dd, 2 H, $C\underline{H}_2Ph$, J_1 = J_2 = 15.0 Hz); 3.73 (ddd, 1 H, H(9), J_1 = J_2 = 10.0 Hz,

J_3 = 3.0 Hz); 7.13 (d, 2 H, Ph, J = 4.0 Hz); 7.20—7.33 (m, 8 H, Ph). ^{13}C NMR, δ: 15.89 (C(10)); 17.11 (C(2)); 22.78 (C(6)); 29.78 (C(11)); 34.63 ($\underline{C}H_2Ph$, J_{C-P} = 62.5 Hz); 35.51 ($\underline{C}H_2Ph$, J_{C-P} = 59.5 Hz); 37.88 (C(3)); 40.00 (C(9), J_{C-P} = 62.4 Hz); 43.18 (C(4)); 43.96 (C(8)); 52.13 (C(5)); 118.26 (C(1)); 126.67, 126.84, 127.35 (C_p); 128.43, 128.64, 128.72, 129.17, 129.62, 129.67 (C_o, C_m); 131.49 (C_{ipso}, J_{C-P} = 6.7 Hz); 131.64 (C_{ipso}, J_{C-P} = 7.0 Hz); 137.26 (C_{ipso}); 204.82 (C(7), J_{C-P} = 11.2 Hz). *Minor isomer.* ^{31}P NMR, δ: 44.51. ^{13}C NMR, δ: 16.88 (C(10)); 17.36 (C(2)); 22.66 (C(6)); 29.78 (C(11)); 34.50 ($\underline{C}H_2Ph$, J_{C-P} = 62.5 Hz); 35.32 ($\underline{C}H_2Ph$, J_{C-P} = 59.5 Hz); 37.71 (C(3)); 41.03 (C(9), J_{C-P} = 61.4 Hz); 43.08 (C(4)); 43.15 (C(8)); 53.51 (C(5)); 118.26 (C(1)); 131.50 (C_{ipso}, J_{C-P} = 6.7 Hz); 131.68 (C_{ipso}, J_{C-P} = 7.0 Hz); 137.73 (C_{ipso}); 205.18 (C(7), J_{C-P} = 10.7 Hz).

(1*R,3*R**)-3-[(3*RS*)-3-Dibenzylphosphinoyl-3-(4-methoxyphenyl)propionyl]-2,2-dimethylcyclobutylacetonitrile (16) (a mixture of epimers, 4 : 1)** was synthesized from unsaturated ketone **11** (0.20 g, 0.71 mmol) as a white crystalline product. The duration of the reaction was 7 h. The yield was 91% (0.33 g), m.p. 140—147 °C (from Bu^{t}OMe). High-resolution mass spectrum. Found: m/z 513.24603. $C_{32}H_{36}O_3PN$. Calculated: M = 513.24327. MS, m/z (I_{rel} (%)): 513 (6), 422(29), 363(22), 327(17), 161(14), 150(49), 139(12), 91(35), 55(100). IR (c 3%, $CHCl_3$), ν/cm^{-1}: 3100—2850 (C—H); 2250 (CN); 1700 (C=O); 1610, 1500, 1200 (P=O); 1030.

NMR spectra (the major isomer). ^{31}P NMR, δ: 43.70. ^{1}H NMR, δ: 0.29 (s, 3 H, H(10)); 1.15 (s, 3 H, H(11)); 1.85 (m, 2 H, H(6)); 2.11 (m, 1 H, H(3)); 2.27 (m, 2 H, H(2)); 2.61 (mdd, 1 H, H(5), $J_1 = J_2$ = 8.0 Hz); 2.69 (dd, 1 H, H(8a), J_1 = 15.0 Hz, J_2 = 11.0 Hz); 2.79 (dd, 1 H, H(8b), $J_1 = J_2$ = 15.0 Hz); 2.96 (dd, 2 H, $C\underline{H}_2Ph$, J_1 = 14.0 Hz, J_2 = 11.0 Hz); 3.06 (dd, 2 H, $C\underline{H}_2Ph$, $J_1 = J_2$ = 14.0 Hz); 3.66 (m, 1 H, H(9)); 3.76 (s, 3 H, OMe); 6.82 (d, 2 H H_o, J = 4.0 Hz); 7.13 (d, 2 H, H_o, J = 4.0 Hz); 7.17—7.30 (m, 6 H, Ph). ^{13}C NMR, δ: 15.95 (C(10)); 17.06 (C(2)); 22.47 (C(6)); 29.74 (C(11)); 34.75 ($\underline{C}H_2Ph$, J_{C-P} = 62.6 Hz); 35.61 ($\underline{C}H_2Ph$, J_{C-P} = 59.1 Hz); 37.83 (C(3)); 39.02 (C(9), J_{C-P} = 63.5 Hz); 43.11 (C(4)); 43.97 (C(8)); 52.95 (C(5)); 55.00 (OMe); 114.05 (C_o); 118.24 (C(1)); 204.89 (C(7), J_{C-P} = 13.7 Hz); 129.54, 131.58, 158.66 (C_{ipso}); 126.57, 126.75, 128.35, 128.57, 129.64, 130.14 (C_o, C_m, C_p).

(1*R,3*R**)-3-[(3*RS*)-3-Dibenzylphosphinoyl-3-(4-dimethylaminophenyl)propionyl]-2,2-dimethylcyclobutylacetonitrile (17) (a mixture of epimers, 4 : 1)** was synthesized from unsaturated ketone **12** (0.70 g, 2.36 mmol) as an orange crystalline product. The duration of the reaction was 12 h. After passing through a layer of Al_2O_3, the yield was 96% (1.04 g), m.p. 145—150 °C (from ethyl acetate). High-resolution mass spectrum. Found: m/z 526.27715. $C_{33}H_{39}O_2PN_2$. Calculated: M = 526.27490. MS, m/z (I_{rel} (%)): 526 (19), 297(80), 174(10), 150(38), 148(58), 147(21), 146(20), 91(19), 55(100). IR (c 3%, $CHCl_3$), ν/cm^{-1}: 3100—2800 (C—H); 2250 (CN); 1700 (C=O); 1610, 1510, 1490, 1150 (P=O).

NMR spectra (the major isomer). ^{31}P NMR, δ: 45.99. ^{1}H NMR, δ: 0.31 (s, 3 H, H(10)); 1.16 (s, 3 H, H(11)); 1.84 (m, 2 H, H(6)); 2.13 (m, 1 H, H(3)); 2.25 (m, 2 H, H(2)); 2.65 (mdd, 1 H, H(5), $J_1 = J_2$ = 8.0 Hz); 2.69 (dd, 1 H, H(8a), J_1 = 15.0 Hz, J_2 = 11.0 Hz); 2.75 (dd, 1 H, H(8b), $J_1 = J_2$ = 15.0 Hz); 2.86 (s, 6 H, NMe_2); 2.91 (dd, 2 H, $C\underline{H}_2Ph$, J_1 = 14.0 Hz, J_2 = 11.0 Hz); 3.04 (dd, 2 H, $C\underline{H}_2Ph$, $J_1 = J_2$ = 14.0 Hz); 3.64 (m, 1 H, H(9)); 6.82 (d, 2 H, H_o, J = 4.0 Hz); 7.13 (d, 2 H, H_o, J = 4.0 Hz); 7.17—7.30 (m, 6 H, Ph). ^{13}C NMR, δ: 16.03 (C(10)); 17.06 (C(2)); 22.45 (C(6)); 29.77 (C(11)); 34.75 ($\underline{C}H_2Ph$, J_{C-P} = 62.6 Hz); 35.61 ($\underline{C}H_2Ph$, J_{C-P} = 59.1 Hz); 37.83 (C(3)); 39.02 (C(9), J_{C-P} = 63.5 Hz); 43.11 (C(4); 43.65 (NMe_2); 43.97 (C(8)); 52.90 (C(5)); 114.05 (C_o); 118.24 (C(1)); 204.89 (C(7), J_{C-P} = 13.7 Hz); 129.54, 131.58, 158.66 (C_{ipso}); 126.57, 126.75, 128.35, 128.57, 129.64, 130.14 (C_o, C_m, C_p).

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