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A novel structural type of conformationally fixed, mixed phosphonium-iodonium ylides based on phenoxaphosphinine

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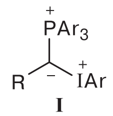
A synthetic approach to a novel type of phosphonium and mixed phosphonium-iodonium ylides containing a conformationally fixed phosphonium fragment is developed. New representatives of these families of chemical compounds based on cyclic phenoxaphosphinine were synthesized. One compound was structurally characterized by single-crystal X-ray diffraction. Based on the ^{1}H NMR data, one can state that phosphonium ylide exists in solution in the form of two geometric isomers even at room temperature. This is indicative of pronounced double-bond character of the bond between the ylide carbon atom and the stabilizing carbomethoxy group.

Keywords: mixed ylides, phosphonium ylides, phosphonium-iodonium ylides, phenoxaphosphinine, cyclic phosphines.

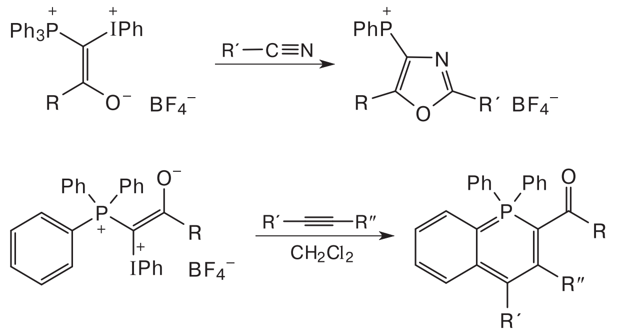
Among a great variety of ylides, mixed phosphonium-iodonium ylides hold a specific place owing to unique synthetic potential originating from two onium fragments and a mesomeric acceptor at the carbanion center (structure I). Nevertheless, they still remain the least studied representatives of this large class of chemical compounds.



I

During the last two decades we have carried out systematic studies on the synthesis and properties of mixed phosphonium-iodonium ylides. In particular, we have for the first time demonstrated that they can enter into heterocyclization reactions with compounds containing both C≡N (see Refs 1, 2) and C≡C bonds (see Refs 3—10) to give heterocyclic systems (Scheme 1).

Scheme 1



Mixed ylides with the phosphonium fragment based on cyclic phosphine derivatives still remain unknown.

The most widely used and the best described cyclic phosphines include phosphole and its benzo analogue, *viz.*, 5-phenyl-5*H*-benzo[*b*]phosphindole (or 5-phenyl-5*H*-dibenzophosphole) where the phosphorus atom is a constituent of the five-membered ring. Recently, such structures have attracted increasing attention as promising organic ligands with unique optical and electronic properties.[11] Systems with the phosphorus atom included in the six-membered ring, *e.g.*, 10-phenyl-10*H*-phenoxaphosphinine (**1**), are much less studied. At present, the 1,4-oxaphosphinine ligands and more complex organic structures containing this fragment are used in homogeneous catalysis as bulky phosphine ligands.[12—15]

This work is a continuation of our research on the synthetic potential of mixed phosphonium-iodonium ylides. Here we report on a previously unknown structural modification of a mixed ylide where the phosphonium moiety adopts a fixed conformation. The synthesis was carried out using 10-phenyl-10*H*-phenoxaphosphinine **1** as the starting substrate.

Compound **1** was synthesized in 25% yield following a classical scheme, *viz.*, by *ortho*-dilithiation of diphenyl ether followed by the reaction of the dilithium derivative with dichlorodiphenylphosphine[16] (Scheme 2).

Phosphonium salt **2** was obtained by alkylation of **1** with methyl bromoacetate. The ^{1}H NMR spectrum of compound **2** exhibits a characteristic doublet of methylene group with a spin-spin coupling constant $^2J_{\mathrm{H,P}}$ of 14.2 Hz. Ylide **3** was obtained by the reaction of salt **2** with sodium methoxide (Scheme 3).

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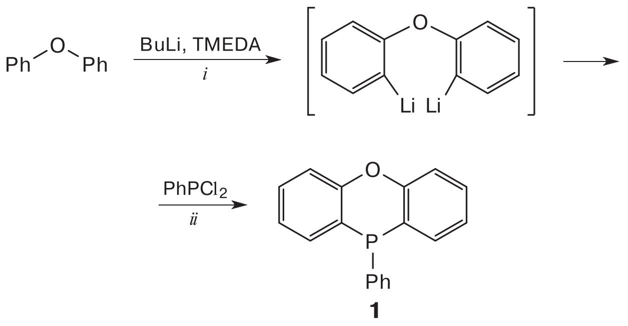
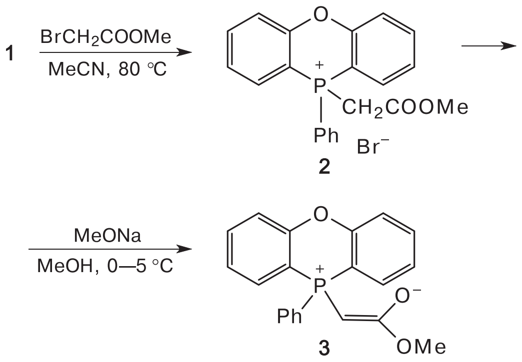
Scheme 2

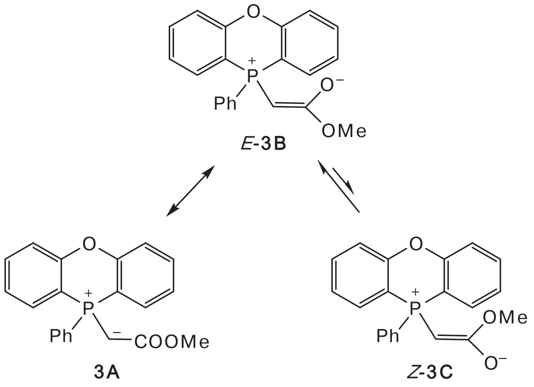


i. Ether, hexane, 0 °C; *ii.* –78 °C.

Scheme 3



Scheme 4



The carbon—carbon bond in the ylides stabilized by mesomeric acceptor substituents has partial double bond character. Various stereoisomers of stabilized ylides were detected at −40 °C by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies.**[17]** The NMR spectra of ylide **3** demonstrate the presence of two geometric isomers even at room temperature. Two doublets at δ 2.77 and 2.96 in the ^{1}H NMR spectrum correspond to proton at the ylide carbon atom while two singlets at δ 3.20 and 3.54 correspond to the methoxy group (Fig. 1). The structure of compound **3** can be described by a number of resonance forms (Scheme 4), and the presence of two isomers in solution suggests the predominant contributions of structures **3B** and **3C**.

To obtain additional information on the structure of ylide **3**, we carried out quantum chemical calculations at the PBE1PBE/dev-2-TZVP level of the density functional theory (DFT). Full geometry optimization of the *E*- and *Z*-isomers with the P(1)—C(1)C(2)=O(2) torsion angle equal to −1.8° and 178.4°, respectively, showed that their energies are comparable (Fig. 2). According to calculations, the energy of the former isomer is 1 kcal mol^{-1} lower than that of the latter; however, taking account of the higher dipole moment of the *Z*-isomer (6.2 D *vs*. 4.16 D), one can assume that both isomers have equal energies in a polar medium. An analysis of the bond lengths showed that this structure is characterized by delocalization of the π-electron density in the P(1)—C(1)C(2)=O(2) fragment with predominant contribution for the P(1)—C(1) bond (1.685—1.687 Å) rather than the C(1)—C(2) bond (1.422—1.427 Å). From these bond length intervals it follows that the change in the type of the isomer does not lead to significant redistribution of the π-electron density. In particular, the C=O bond length changes from 1.212 to 1.222 Å. A scan of the potential energy surface along the P(1)—C(1)—C(2)—O(2) coordinate showed that, owing to a small contribution of π-bonding to the C(1)—C(2) bond, the barrier to rotation about this bond is 10.5 kcal mol^{-1}. The maximum energy value was obtained for the structure with a torsion angle of 101.6°. The C(1)—C(2) bond length varied only slightly (from 1.42 to 1.44 Å) on scanning.

Phosphorane **3** was oxidized by (diacetoxyiodo)benzene in methanol to phosphonium-iodonium ylide **4** (Scheme 5). Usually, crystalline mixed ylides contain counterions with no nucleophilic properties. Ylide **4** can be stabilized by adding HBF_4 and HPF_6 to the reaction mixture to give compounds **4a** and **4b**, respectively. Note that precipitation of **4a** occurs within a few minutes (the yield is 48%) while ylide **4b** precipitates immediately (the yield is 56%). The presence of the BF_4^- and PF_6^- counterions in the mixed ylides was proved by IR spectroscopy and by ^{19}F and ^{31}P NMR spectroscopies (for PF_6^-). The ^{1}H NMR spectrum of the carbomethoxy-substituted mixed ylide **4** exhibits a characteristic broadening of the signal of the methoxy group.**[18]** It follows that this signal is a superposition of signals from two geometric isomers similar to those of ylide **3**; however, the barrier to rotation about the bond formed by the ylide carbon atom and the carboxyl group at room temperature is almost overcome. A similar picture was observed earlier for mixed phosphonium-iodonium ylides**[19]** and products of their nucleophilic substitution.**[18]**

Our previous studies revealed that crystalline mixed phosphonium-iodonium ylides are stable and slowly de-

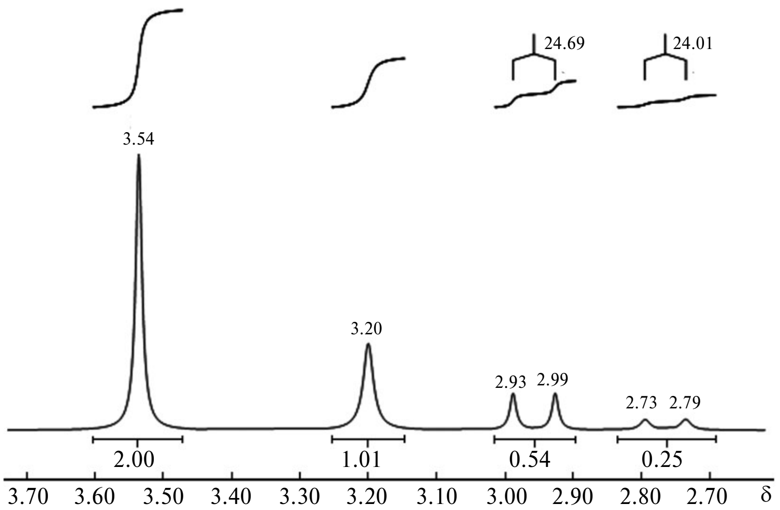
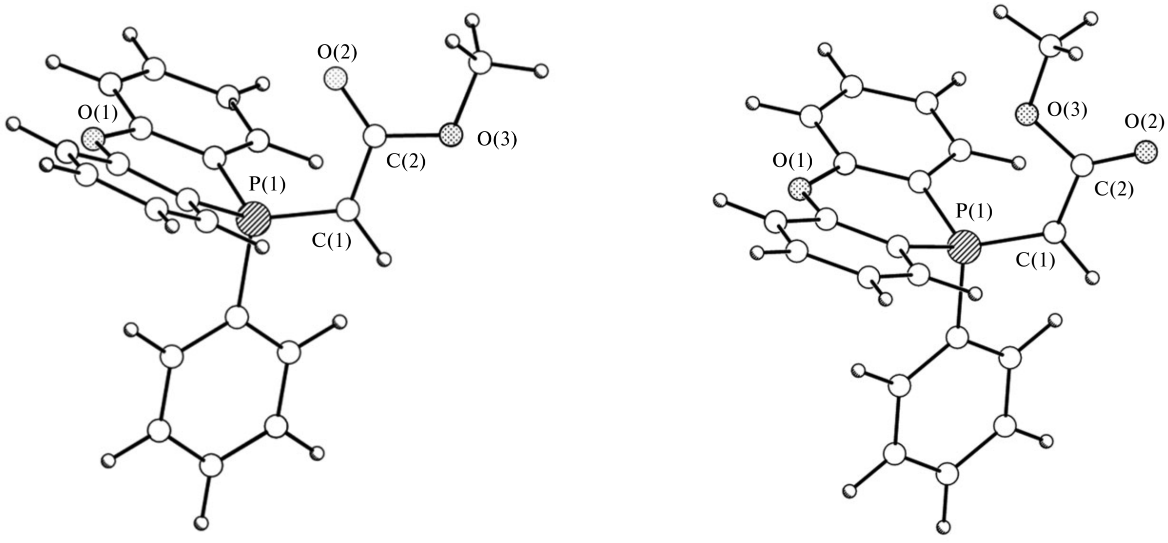


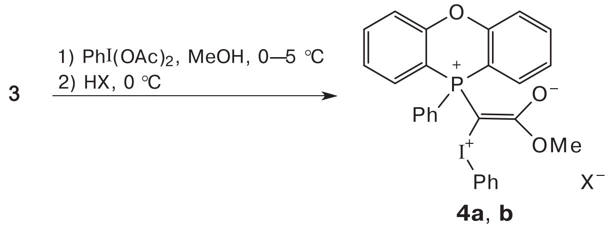
Fig. 1. A fragment of the ^{1}H NMR spectrum of compound **3**.



E *Z*

Fig. 2. *E*- and *Z*-isomers of **3**: a general view (obtained from PBE1PBE/def-2-TZVp calculations).

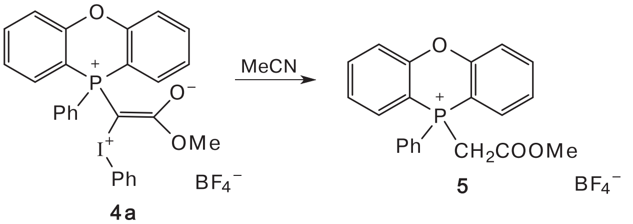
Scheme 5



compose in solvents by homolytic dissociation of the C—I bond resulting in corresponding phosphonium salts.[20—22]

Taking ylide **4a** as an example, we demonstrated that the novel conformationally fixed phosphonium-iodonium ylides are also transformed to salts on long-term standing in solution; the process proceeds faster on UV irradiation (Scheme 6).

Scheme 6



The structure of the phosphonium salt **5** was confirmed by single-crystal X-ray diffraction (Fig. 3, Tables 1 and 2).

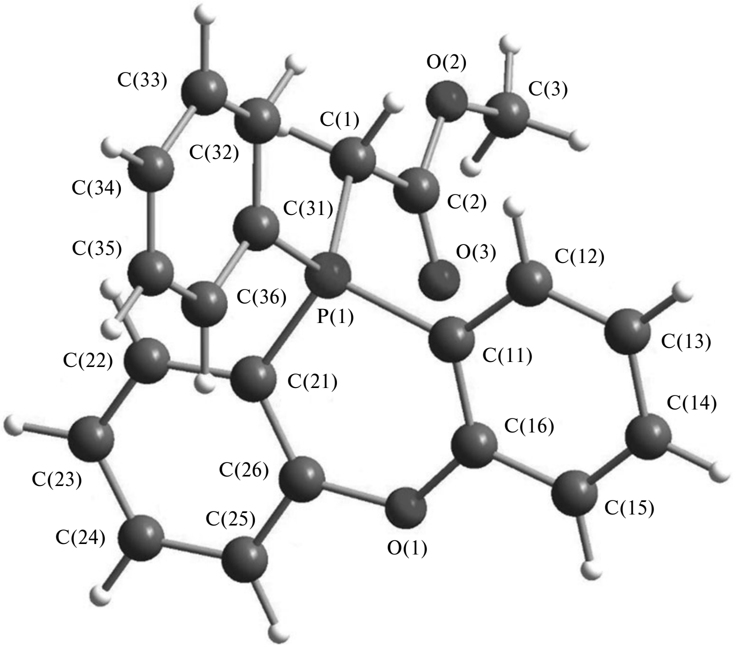


Fig. 3. Molecular structure of phosphonium cation in salt **5**.

The central ring in the cation is almost planar. The maximum deviation of the P(1) atom from the plane where other atoms lie, is 0.12 Å. The P(1)—C(1) bond (1.791(4) Å) is much longer than the corresponding bond in the *E*- and *Z*-isomers **3** (see above). The C(16)—O(1) and C(26)—O(1) bond lengths are close (1.361(4) *vs.* 1.368(4) Å), being almost equal to the average bond lengths in xanthenes. By and large, the most important bond lengths and bond angles in the cation of salt **5** are close to those in 10-methyl-10-phenyl-10*H*-phenoxaphosphonium bromide[23] and 10-(4-bromobenzyl)-10-phenyl-10*H*-phenoxaphosphonium bromide.[24]

Summing up, we developed a synthetic approach to a novel type of phosphonium and mixed phosphonium-iodonium ylides containing a conformationally fixed phosphonium fragment. Based on the ^{1}H NMR data, one can state that phosphonium ylide **3** exists in solution in the form of two geometric isomers even at room temperature. This is indicative of pronounced double-bond character of the bond between the ylide carbon atom and the stabilizing carbomethoxy group.

Table 1. Selected interatomic distances (*d*) in compound **5**

Bond	*d*/Å	Bond	*d*/Å
P(1)—C(1)	1.791(4)	C(21)—C(22)	1.392(4)
P(1)—C(11)	1.757(3)	C(21)—C(26)	1.387(5)
P(1)—C(21)	1.763(3)	C(25)—C(26)	1.388(5)
P(1)—C(31)	1.786(3)	C(26)—O(1)	1.368(4)
C(11)—C(12)	1.400(4)	C(1)—C(2)	1.504(5)
C(11)—C(16)	1.391(4)	C(2)—O(2)	1.306(5)
C(15)—C(16)	1.393(5)	C(2)—O(3)	1.180(5)
C(16)—O(1)	1.361(4)	C(3)—O(2)	1.453(8)

Table 2. Selected bond angles (ω) in compound **5**

Angle	ω/deg
C(1)—P(1)—C(11)	110.93(15)
C(11)—P(1)—C(21)	103.81(14)
C(11)—P(1)—C(31)	110.91(14)
C(21)—P(1)—C(31)	110.79(14)
P(1)—C(11)—C(16)	120.6(2)
P(1)—C(21)—C(26)	120.5(2)
C(11)—C(16)—O(1)	124.8(3)
C(21)—C(26)—O(1)	124.9(2)
C(16)—O(1)—C(26)	124.8(2)

Experimental

Quantum chemical calculations were carried out within the framework of dispersion corrected DFT using the PBE0 functional,[25] the def-2-TZVP basis set, and the Gaussian09 program.[26] Geometry optimization was performed taking account of empirical dispersion correction to the total energy[27] with the D3 damping function by Becke and Johnson.[28]

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM-400 and Agilent 400-MR spectrometers, both operating at 400, 100, and 162 MHz, respectively. The solvent signals were used as internal references, *viz*., δ 7.26 ($CDCl_3$) and δ 2.49 (DMSO-d_6) for ^{1}H and δ 77.1 ($CDCl_3$) and δ 39.5 (DMSO-d_6) for ^{13}C; 85% H_3PO_4 was used as external reference for ^{31}P.

Infrared spectra were recorded on a Thermo Scientific Nicolet IR200 FT IR spectrometer equipped with an attenuated total reflection (ATR) accessory with a ZnSe crystal. The angle of incidence was 45° and the spectral resolution was 4 cm^{-1}. A total of 20 scans were collected.

High-resolution electrospray ionization (ESI) mass spectra were recorded on an Agilent LC/MSD 1100 SL instrument with atmospheric pressure ESI (AP-ESI) in the positive ion mode (ion trap mass analyzer). Conditions: drying gas (nitrogen) temperature 300 °C; drying gas feed rate 12 L min^{-1}, ion source voltage 5000 V, capillary voltage 150 V, acetonitrile as solvent.

Chromatography. Chromatographic separation was performed using columns filled with MN Kieselgel 60 silica gel (0.04—0.063 mm//230—400 mesh ASTM).

10-Phenyl-10*H*-phenoxaphosphinine[16] (1). Glassware was dried in a vacuum oven. The synthesis was carried out in a dry argon atmosphere. Diphenyl ether (12.32 g, 0.072 mol) was dissolved in dry hexane—diethyl ether mixture (1 : 1 v/v, a total volume of 360 mL) and freshly distilled TMEDA (25.9 mL, 0.174 mol) was added. The reaction mixture was cooled to 0 °C and 2.5 *M* Bu^nLi in hexane (69.5 mL, 0.174 mol) was added dropwise with stirring. The mixture was stirred for 8 h at room temperature, cooled to –78 °C, and dichlorodiphenylphosphine (14.7 mL, 0.109 mol) was added dropwise. The reaction mixture was stirred for 10 h at room temperature, distilled water (150 mL) was added, then extracted with ether (3×50 mL), washed with saturated aqueous NaCl solution (70 mL), and dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure, the residue was chromatographed on silica gel using petroleum ether as eluent and then recrystallized from hot petroleum ether. The yield was 5.00 g (25%), white crystals. ^{1}H NMR ($CDCl_3$), δ: 7.15 (tt, 2 H, H_{arom}, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.3 Hz); 7.22 (m, 7 H, H_{arom}); 7.39 (ddd, 2 H, H_{arom}, $^3J_{H,P}$ = 8.8 Hz, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.7 Hz); 7.52 (ddd, 2 H, H_{arom}, $^3J_{H,P}$ = 10.4 Hz, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.7 Hz). ^{31}P NMR ($CDCl_3$), δ: – 54.37.

10-(2-Methoxy-2-oxoethyl)-10-phenyl-10*H*-phenoxaphosphonium bromide (2). To a solution of 10-phenyl-10*H*-phenoxaphosphinine **1** (0.64 g, 2.3 mmol) in acetonitrile (3 mL), methyl bromoacetate (0.23 mL, 2.4 mmol) was added. The mixture was stirred on heating (80 °C) for 2 h. The precipitate was filtered off, washed with acetonitrile (3×2 mL), then with diethyl ether (2 mL), and dried at room temperature. The yield was 0.63 g (63%), white crystals, m.p. 130—132 °C. ^{1}H NMR (DMSO-d_6), δ: 3.49 (s, 3 H, OCH_3); 5.33 (d, 2 H, $C\underline{H}_2COOMe$, $^2J_{P,H}$ = 14.2 Hz); 7.52—7.60 (m, 2 H, H_{arom}); 7.66—7.72 (m, 2 H, H_{arom}); 7.73—7.79 (m, 2 H, H_{arom}); 7.84—7.90 (m, 1 H, H_{arom}); 7.94—8.05 (m, 6 H, H_{arom}). ^{13}C NMR (DMSO-d_6), δ: 30.98 (d, CH_2, $^1J_{C,P}$ = 50.6 Hz); 53.20 (s, OMe); 98.15 (d, C_{ipso}, $^1J_{C,P}$ = 92.7 Hz); 119.31 (d, $J_{C,P}$ = 6.1 Hz); 121.05 (d, C_{ipso}, $^1J_{C,P}$ = 97.1 Hz); 125.78 (d, $J_{C,P}$ = 11.8 Hz); 130.16 (d, $J_{C,P}$ = 14.2 Hz); 132.24 (d, $J_{C,P}$ = 7.7 Hz); 133.36 (d, $J_{C,P}$ = 12.4 Hz); 135.38 (d, $J_{C,P}$ = 2.6 Hz); 137.56 (s, C_{arom}); 155.73 (s, C_{arom}); 165.15 (d, C=O, $^2J_{C,P}$ = 3.7). ^{31}P NMR (DMSO-d_6), δ: –8.96. IR, ν/cm^{-1}: 1720 (COOMe). High-resolution ESI mass spectrum: found *m/z* 349.0985 $[M]^+$; calculated for $C_{21}H_{18}O_3P^+$ 349.0988.

Methyl-2-(10-phenyl-10*H*-10λ^5-phenoxaphosphinine-10-ylidene) acetate (3). To a solution of phosphonium salt **2** (0.60 g, 1.4 mmol) in anhydrous methanol (4 mL), a solution of sodium methoxide (0.076 g, 1.4 mmol) in anhydrous methanol (1 mL) was added gradually, the temperature of the reaction mixture being maintained at 0—5 °C. As the whole amount of sodium methoxide was added, white precipitate disappeared. The reaction mixture was stirred for 1 h, methanol was removed at reduced pressure at room temperature, and the residue was dissolved in methylene chloride (5 mL). The sodium bromide residue was separated from the solution of ylide **3** by filtering, and filter-washed with methylene chloride (3×5 mL). The filtrate was concentrated at reduced pressure at room temperature. The yield was 0.43 g (89%), beige-colored crystals, m.p. 130—132 °C. ^{1}H NMR ($CDCl_3$), δ: 2.77, 2.96 (both d, 1 H, $PC\underline{H}$, $^2J_{H,P}$ = = 23.5 Hz, $^2J_{H,P}$ = 24.7 Hz); 3.20, 3.54 (both s, 3 H, Me); 7.20—8.00 (m, 13 H, H_{arom}). ^{13}C NMR ($CDCl_3$), δ: 27.39, 28.87 (both d, CH, $^1J_{C,P}$ = 136.7 Hz; $^1J_{C,P}$ = 129.0 Hz); 49.25, 49.51 (both s, OMe); 109.55 (d, C_{ipso}, $^1J_{C,P}$ = 92.5 Hz); 118.03 (d, $J_{C,P}$ = 5.7 Hz); 124.13 (d, $J_{C,P}$ = 11.8 Hz); 128.60 (d, $J_{C,P}$ = 12.4 Hz); 131.00 (d, $J_{C,P}$ = 10.3 Hz); 131.14 (d, $J_{C,P}$ = 7.2 Hz); 131.59 (d, $J_{C,P}$ = 2.8 Hz); 133.35 (s); 156.27 (s) (C_{arom}); 171.05, 171.18 (both s, C—O^-). ^{31}P NMR ($CDCl_3$), δ: –12.61, –11.63. IR, ν/cm^{-1}: 1622 (COOMe). High-resolution ESI mass spectrum: found *m/z* 349.0983 $[M + H]^+$; calculated for $C_{21}H_{17}O_3P$ 349.0988.

Synthesis of phosphonium-iodonium ylides 4a,b. To a solution of ylide **3** (0.21 g, 0.6 mmol) in methanol (1 mL) cooled to 0 °C, a solution of (diacetoxyiodo)benzene (0.19 g, 0.6 mmol) in methanol (1.5 mL) was added, the temperature of the reaction mixture being maintained at 0 °C. The reaction mixture was stirred for 1 h. Then, a 50% aqueous HBF_4 solution (0.79 mL, 0.6 mmol) (for mixed ylide **4a**) or a 60% HPF_6 solution (0.09 mL, 0.6 mmol) (for ylide **4b**) was added, the temperature being maintained at 0 °C. The solution was stirred for 1 h, diethyl ether (1.5 mL) was added, and stirred for an additional 1 h. The precipitate was filtered off, washed with diethyl ether (3×2 mL), and dried in air.

[2-Methoxy-2-oxo-1-(10-phenyl-10*H*-10λ^5-phenoxaphosphinine-10-ylidene)ethyl](phenyl)iodonium tetrafluoroborate (4a). The yield was 48%, white crystals, decomp. at 125—127 °C. ^{1}H NMR (DMSO-d_6), δ: 3.51 (br.s, 3 H, OMe); 7.39—7.71 (m, 15 H, H_{arom}); 7.76 (t, 1 H, H_{arom}, *J* = 7.6 Hz); 7.84 (t, 2 H, H_{arom}, *J* = 8.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 52.65 (s, OMe); 106.59 (d, C_{ipso}, $^1J_{C,P}$ = 95.4 Hz); 119.42 (d, $J_{C,P}$ = 6.1 Hz); 119.84 (d, $J_{C,P}$ = 3.1 Hz); 124.50 (d, C_{ipso}, $^1J_{C,P}$ = 101.5 Hz); 125.71 (d, $J_{C,P}$ = 11.4 Hz); 130.17 (d, $J_{C,P}$ = 13.0 Hz); 131.66 (s, C_{arom}); 131.76 (s, C_{arom}); 132.38 (d, $J_{C,P}$ = 6.1 Hz); 132.78 (s, C_{arom}); 133.12 (d, $J_{C,P}$ = 11.4 Hz); 134.36 (d, $J_{C,P}$ = 3.0 Hz); 136.34 (d, $J_{C,P}$ = 1.5 Hz); 155.85 (d, $J_{C,P}$ = 2.3 Hz); 167.41 (d, C=O, $^2J_{C,P}$ = 15.3 Hz). ^{19}F NMR (DMSO-d_6), δ: –148.30 $[^{11}BF_4]^-$, –148.25 $[^{10}BF_4]^-$. ^{31}P NMR (DMSO-d_6), δ: –2.99. IR, ν/cm^{-1}: 1600 (COOMe); 1060, 1030 (BF_4^-). High-resolution ESI mass spectrum: found *m/z* 551.0264 $[M]^+$; calculated for $C_{27}H_{21}IO_3P$ 551.0268.

[2-Methoxy-2-oxo-1-(10-phenyl-10*H*-10λ^5-phenoxaphosphinine-10-ylidene)ethyl](phenyl)iodonium hexafluorophosphate (4b). The yield was 56%, white crystals, decomp. at 129—131 °C. ^{1}H NMR (DMSO-d_6), δ: 3.51 (br.s, 3 H, OMe); 7.39—7.71 (m, 15 H, H_{arom}); 7.76 (t, 1 H, H_{arom}, *J* = 7.6 Hz); 7.84 (t, 2 H, H_{arom}, *J* = 8.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 52.65 (s, OMe); 106.59 (d, C_{ipso}, $^1J_{C,P}$ = 95.4 Hz); 119.42 (d, $J_{C,P}$ = 6.1 Hz); 119.84 (d, $J_{C,P}$ = 3.1 Hz); 124.50 (d, C_{ipso}, $^1J_{C,P}$ = 101.5 Hz); 125.71 (d, $J_{C,P}$ = 11.4 Hz); 130.17 (d, $J_{C,P}$ = 13.0 Hz); 131.66 (s, C_{arom}); 131.76 (s, C_{arom}); 132.38 (d, $J_{C,P}$ = 6.1 Hz); 132.78 (s, C_{arom}); 133.12 (d, $J_{C,P}$ = 11.4 Hz); 134.36 (d, $J_{C,P}$ = 3.0 Hz); 136.34 (d, $J_{C,P}$ = 1.5 Hz); 155.85 (d, $J_{C,P}$ = 2.3 Hz); 167.41

(d, C=O, $^2J_{C,P}$ = 15.3 Hz). ^{19}F NMR (DMSO-d$_6$), δ: –70.16 (d, $^1J_{F,P}$ = 711.1 Hz). ^{31}P NMR (DMSO-d$_6$), δ: –144.24 (septet, $^1J_{F,P}$ = 711.6 Hz), –2.97. IR, ν/cm^{-1}: 1610 (COOMe); 840, 830 (PF_6^-). High-resolution ESI mass spectrum: found *m/z* 597.0475 [M]$^+$; calculated for $C_{32}H_{23}IO_2P$ 597.0475.

10-(2-Methoxy-2-oxoethyl)-10-phenyl-10*H*-phenoxaphosphonium tetrafluoroborate (5). A solution of ylide **4a** (0.05 g, 0.078 mmol) in 5 mL of acetonitrile (HPLC) in a quartz tube in dry argon atmosphere was irradiated with a mercury lamp (λ = 365 nm) for 2 h. The ylide conversion was 100%, as determined analyzing the reaction mixture by ^{31}P NMR spectroscopy. After two days, colorless crystals formed on the tube wall. A crystal was picked up and characterized by X-ray diffraction. Other crystals were characterized by ^{31}P NMR spectroscopy. ^{31}P NMR (CDCl$_3$), δ: –9.14.

X-ray diffraction study of phosphonium salt 5. At 295 K: crystals of **5**, $C_{21}H_{18}BF_4O_3P$, are colorless, monoclinic, space group $P2_1/n$, a = 8.7197(15), b = 22.203(5), c = 11.1958(18) Å, β = 105.174(13)°, V = 2092.0(7) Å^3, Z = 4 (Z' = 1), d_{calc} = = 1.384 g cm^{-3}, M = 436.1, μ(Cu-Kα) = 16.68 cm^{-1}, F(000) = 896. The intensities of 2600 reflections were measured on a CAD-4 diffractometer at 298 K (λ(Cu-Kα) = 1.54178 Å, ω/θ-scan, θ < 50°) and 2136 independent reflections (R_{int} = 0.0220) were used for structure refinement. The absorption correction was applied empirically. The transmission factor (min/max) was 0.816/1.000, the θ range was from 2 to 50°, the h, k, l index ranges were as follows: $-8 \le h \le 8$, $-2 \le k \le 22$, and $0 \le l \le 11$; structure refinement based on $|F^2|$. The structure was solved by the direct method using the SIR2002 software package[29] and successive electron density syntheses. The difference Fourier synthesis of the electron density revealed pronounced maxima in the vicinity of the boron atom, which was interpreted as the second position of the BF$_4$ group. Positions of all hydrogen atoms were calculated geometrically and refined using the riding model. Structure refinement on F^2_{hkl} was carried out in the anisotropic approximation for the non-hydrogen atoms and in the isotropic approximation for the hydrogen atoms. The final R-index values for **5**: R_1 = 0.0478 (based on F_{hkl} for 1883 reflections with $I > 2\sigma(I)$), wR_2 = 0.1550, GOOF = 1.10. Calculations were carried out using the JANA 2000 software package.[30] A complete set of structural data for compound **5** was deposited at the Cambridge Crystallographic Data Centre (CCDC 1987446).

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