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Cascade reactions of nitrogen- and phosphorus-containing ylides with methyl diazoacetate and *in situ* generated diazocyclopropane

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Reactions of pyridinium or phosphorus ylides with diazo esters are multistep processes. The first step is covalent bonding between the ylide C atom and the terminal N atom. This is followed by elimination of the ylide-forming molecule and successive addition of one or two ylide fragments. Depending on the nature of the starting reagents, this type of transformations leads to novel polyfunctional phosphorus ylides or, with pyridinium ylides, to polyalkyl 3,4(4,5)-diazaalkadienetri- or tetracarboxylates. A reaction of the *in situ* generated diazocyclopropane with methyl triphenylphosphoranylideneacetate stops at the first step, giving a cyclopropylazo-containing ylide. Reactions of the latter with acyl chlorides yield six-membered heterocyclic betaines with a triphenylphosphonium substituent.

Key words: diazo compounds, pyridinium ylides, phosphoranylidenes, diazadienes, azines, heterocyclization.

Earlier,[1] we have found that carbene decomposition of methyl diazoacetate in boiling pyridine unexpectedly yields tetramethyl tetrahydropyridazine-3,4,5,6-tetracarboxylate (**1**) as a mixture of two geometrical isomers. Under more drastic conditions (boiling xylene in the presence of pyridine), tetramethyl pyrroletetracarboxylate (**2**) has been isolated as the major reaction product. Presumably, these heterocyclic compounds can form *via* generation of intermediate pyridinium ylides followed by their reactions with a diazo compound.[1] To verify this assumption, we have studied[2] reactions of alkyl diazoacetates with pyridinium ylides generated from other precursors (*e.g.*, quaternary pyridinium salts prepared from haloacetic acid esters proved to be convenient precursors of such ylides[3]).

In fact, reactions of alkyl diazoacetates with pyridinium methoxycarbonylmethylide (**3a**) generated by decomposition of a pyridinium salt with K_2CO_3 ultimately afforded the same heterocycles **1** or **2** in 40—70% yields (Scheme 1).[2] The reaction rate and pathway depend on both the polarity of the medium and the temperature. This allowed us to isolate two novel acyclic intermediates **4** and **5** that are precursors of compounds **1** and **2**. Rearrangement of azine **4** into diazadiene **5** followed by cyclization of the latter into tetrahydropyridazine **1** are accelerated by bases or polar solvents.

Using the starting compounds with different ester groups, *e.g.*, (methoxycarbonyl)methylpyridinium iodide and ethyl diazoacetate, we found, from the numbers of the COOMe and COOEt groups in reaction products, that the formation of diazadienes **4** and **5** involves three ylide molecules and only one diazo ester molecule.[2] These results motivated us to study in more detail reactions of diazo compounds with ylides.

Results and Discussion

Previously,[2] we have determined only the final steps of multistep reactions of diazoacetate with ylides that first give rise to open structures **4** and **5** and then to heterocyclic tetraesters **1** or **2**. Here we tried to elucidate the character of cascade transformations during reactions of diazo compounds with ylides. In the hope of isolating products characteristic of the earlier steps of this process, we varied the nature (and, accordingly, reactivities) of the starting reagents, first of all by employing less reactive ylides such as normally stable methyl triphenylphosphoranylideneacetate (**3b**) and sterically hindered pyridinium methoxycarbonyl(phenyl)methylide (**6**).

In chloroform at 25 °C, methyl diazoacetate reacted only with two molecules of ylide **3b** to give triphenylphosphoranyl derivative **7b**. This compound was isolated in the individual state and structurally characterized by X-ray diffraction analysis and NMR spectroscopy. In the crystal structure of this phosphorane, the vicinal ester groups are *trans* to each other (Scheme 2). The length of the ylide P—C bond is 0.169 nm.

^{1}H NMR study of compound **7b** revealed its existence in solution predominantly as two isomers, their ratio depending on the solvent polarity and the temperature. For

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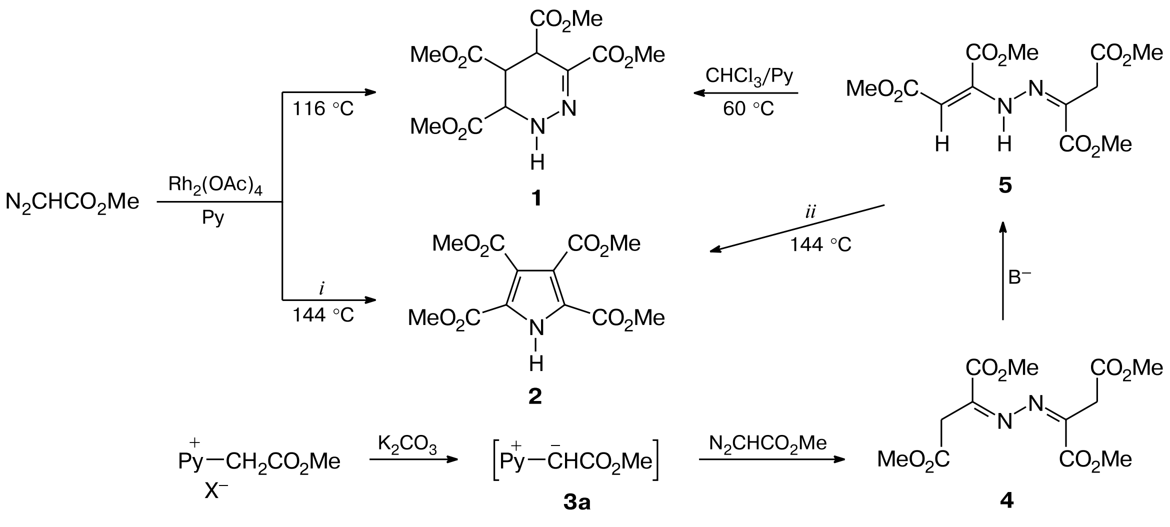
Scheme 1



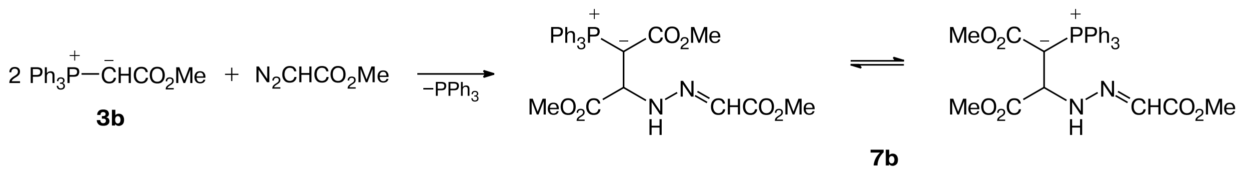
i. Xylene. *ii*. Py/xylene.

instance, in $CDCl_3$ at 20 °C, the signals for the vinyl proton and the ester group at the ylide C atom appear as two pairs of singlets in the ratio 1 : 2.2, while the signal for the methine proton is a poorly resolved multiplet. The ^{31}P NMR spectrum also contains two closely spaced signals (δ_P 23.5 and 22.4) with approximately the same ratio of their integral intensities. However, at 55 °C, the corresponding signals for the =CH and COOMe fragments coalesce into single signals at δ 6.70 and 3.28, respectively, while the multiplet for the methine proton changes into a doublet of doublets. The spin-spin coupling constants $^3J_{HCNH}$ and $^3J_{HP}$ determined from a decoupling experiment are 7.3 and 16.4 Hz, respectively. The simplification of the spectrum observed at elevated temperature can be attributed either to accelerated interconversions of two conformers (arising from hindered rotation about the C—C bond between the ylide and chiral carbon atoms) or to interconversions of the *syn*- and *anti*-isomers relative to the C=N bond (*cf.* Ref. 4), which results in the coalescence of the signals in the spectrum. At −30 °C, the appearance of the spectrum changes only slightly. The signal intensity ratio for the ester groups remains virtually unchanged, while the signal for the methine proton becomes much broader, almost coalescing with the basic line. The original spectral pattern is resumed on warming or cooling of the samples to 20 °C; this is unambiguous evidence for dynamic equilibrium most likely associated with hindered rotation of some fragments of the molecule. Analogous splitting of the signals is observed in the ^{13}C and ^{31}P NMR spectra of compound **7b**.

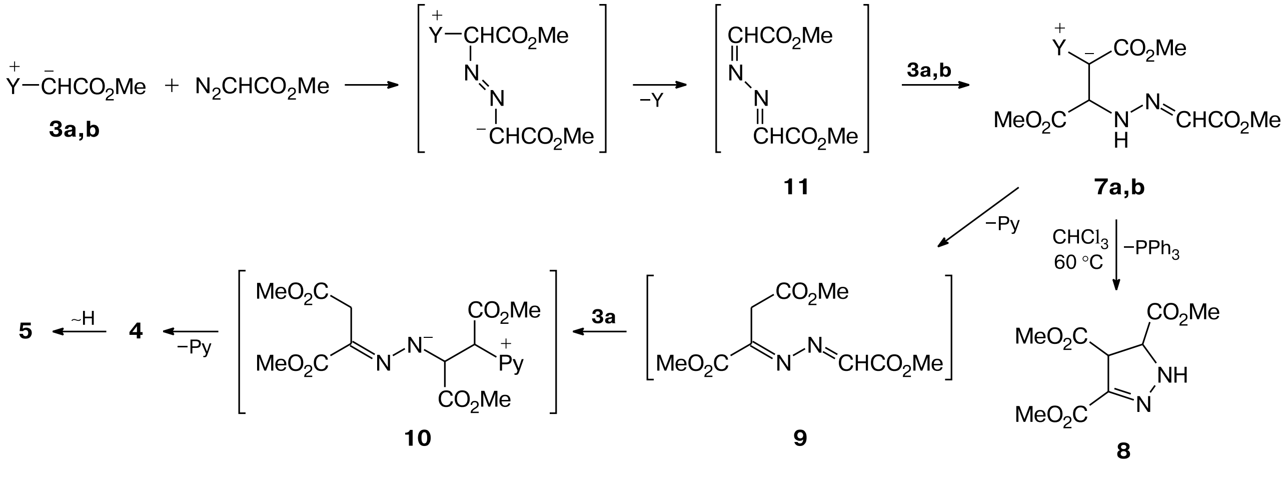
We also studied the dependence of the conformational equilibrium on the solvent polarity. It turned out that in polar solvents, the difference between the integral intensities of the signals for similar protons in two conformers of compound **7b** is smaller (~1 : 1.3 in DMSO or acetone and 1 : 1 in acetonitrile). In both cases, the protons of two ester groups whose signals coincide in $CDCl_3$ (δ 3.72) have different chemical shifts, while the signal for NH is shifted downfield, leaving the range of aromatic protons.

As expected, phosphorus-containing ylide **7b** is more stable than the corresponding pyridinium ylide **7a**, which eliminates pyridine under the reaction conditions and hence cannot be detected. Nevertheless, when refluxed in $CHCl_3$ for 6 h, compound **7b** loses triphenylphosphine to give 3,4,5-trimethoxycarbonyl-2-pyrazoline (**8**) in almost quantitative yield (Scheme 3). Compound **8** is analogous to the product of 1,3-dipolar cycloaddition of methyl diazoacetate to methyl fumarate.[5] In the former case, easy elimination of the pyridine molecule leads to azine **9**,

Scheme 2



Scheme 3



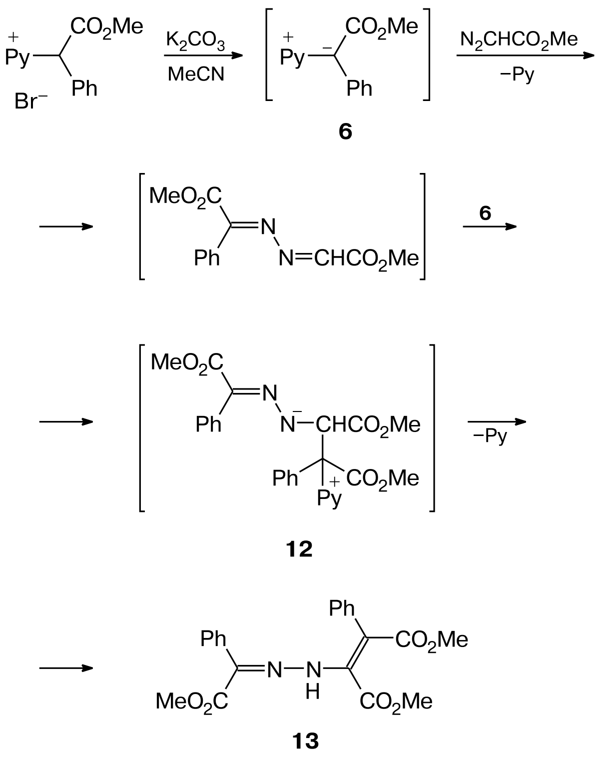
Y = Py (**a**), PPh_3 (**b**)

which immediately reacts with ylide **3a** to give novel ylide **10**. In the latter case, the driving force of the reaction is probably cyclization of ylide **7b** into a five-membered heterocycle accompanied by elimination of triphenylphosphine to form pyrazoline **8**.

The structure of phosphorane **7b** containing the 3,4-diazahex-2-en-5-yl substituent suggests the formation of unstable intermediate azine **11** from phosphorane **3b** and methyl diazoacetate with elimination of PPh_3 (see Scheme 3). Such a transformation has been assumed earlier[6] for a reaction of benzylidene(triphenyl)phosphorane with diazoacetophenone, which gave the corresponding azine as the final product because it was unable to react with benzylidene(triphenyl)phosphorane.

In the reaction of methyl diazoacetate with sterically hindered pyridinium methoxycarbonyl(phenyl)methylide (**6**) (generated from the corresponding quaternary pyridinium salt in the presence of K_2CO_3 in acetonitrile at 20 °C), the diazo compound successively interacts with two ylide molecules and the process stops as well (Scheme 4). Intermediate betaine **12** is converted, through the loss of the pyridine molecule, into stable ene hydrazone **13**, which is inert toward ylide **6** and isolated from the reaction mixture as a crystalline product in ~60% yield.

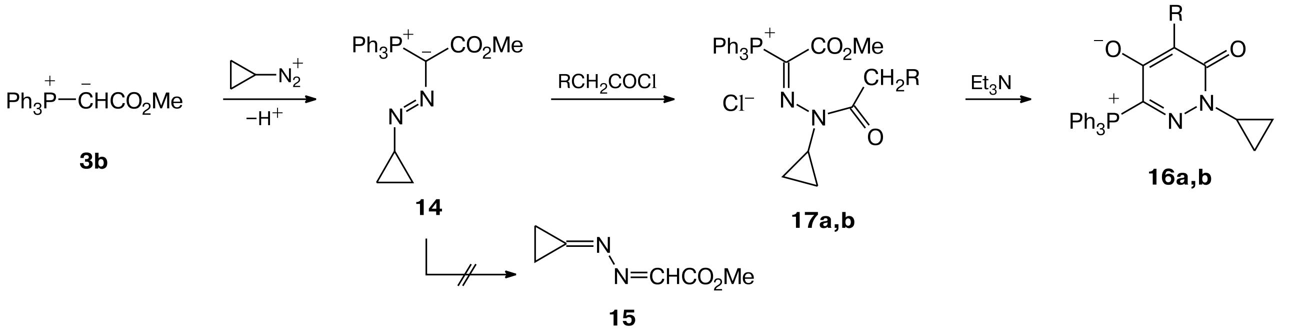
Scheme 4



Thus, the degree of sequential transformations in reactions of diazo carbonyl compounds with ylides is largely affected by the polarization of both the ylide fragment and the diazo group. On the one hand, the extent of the observed cascade transformations depends on the ease of elimination of the ylide-forming molecule (PPh_3 or pyridine); on the other hand, on the reactivities of intermediate azines, for which the presence of an electron-deficient site and the absence of steric hindrances are substantial. Both these factors are also important for cyclization of hydrazones of the type **5** into, *e.g.*, tetrahydropyridazines **1**. For instance, hydrazones that are structurally close to compound **5** but contain no activating groups do not undergo such a cyclization.[7]

A reaction of phosphorane **3b** with *in situ* generated diazocyclopropane is of certain interest. In contrast to reactions with diazo esters, this reaction affords only cyclopropylazo phosphorane **14** (Scheme 5). Com-

Scheme 5



R = Cl (**a**), Ph (**b**)

pound **14** was isolated as yellow crystals in 78% yield and proved to be very stable (m.p. 184—185 °C). Its high stability is probably due to the impossibility of eliminating triphenylphosphine, which would give rise to unstable compound **15**. Essentially, the observed reaction is analogous to reactions of phosphorane **3b** with aryldiazonium salts,[8] which suggests addition to ylide of the cyclopropyldiazonium ion rather than diazocyclopropane itself.

Recently,[9,10] we have demonstrated that the cyclopropyldiazonium ion is really generated from *N*-cyclopropyl-*N*-nitrosourea and K_2CO_3 and can participate in C-azo coupling with some substrates, in particular β-diketones, to give the corresponding cyclopropylazo compounds or cyclopropylhydrazones. Note that neither phosphorane **3b** nor pyridinium ylides **3a** and **6** react with diazomethane or phenyldiazomethane, which is undoubtedly associated with much lower polarization of the diazo group in diazoalkanes compared to diazo carbonyl compounds and especially diazonium ions.

We also found that ylide **14** can serve as an interesting synthon for the synthesis of cyclopropyl-containing heterocycles. For instance, acylation of azo phosphorane **14** with chloro- or phenylacetic acid chlorides in CH_2Cl_2 in the presence of triethylamine gives heterocyclic betaines **16a,b** in 57—60% yields. Apparently, the latter form as the result of an electrophilic attack on the N atom followed by cyclization of salt **17** under the action of triethylamine.

Thus, diazo compounds containing electron-withdrawing groups can react with some N- and P-containing ylides in a cascade fashion; the first step involves covalent bonding between the ylide C atom and the terminal N atom. This is followed by elimination of the ylide-forming molecule (pyridine or PPh_3) and by addition of one or two more ylide fragments to the electron-deficient C atoms of intermediate diazadienes. These transformations afford polyalkyl 3,4(4,5)-diazaalkadienetri- or tetracarboxylates, tetrahydropyridazine derivatives, or novel polyfunctional phosphorus ylides. Diazocyclopropane generated by alkaline decomposition of *N*-cyclopropyl-*N*-nitrosourea reacts with phosphoranylideneacetate probably as the cyclopropyldiazonium ion to give stable (cyclopropylazo)phosphoranylideneacetate. The compounds obtained are of interest for the synthesis of polyfunctional heterocyclic compounds.

Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM-300 (300.13 (^1H), 75.5 (^{13}C), and 121.49 MHz (^{31}P)) and Bruker DRX-500 spectrometers (500.13 MHz) in $CDCl_3$ with Me_4Si (0.05%) as the internal standard; δ_P are referenced to H_3PO_4. ^{13}C NMR spectra were recorded with broad-band proton decoupling. Mass spectra were recorded on Finnigan MAT INCOS-50 (EI, 70 eV, direct inject probe) and Finnigan LCQ instruments (ESI). IR spectra were recorded on a Bruker IFS-113v instrument (as solutions in CCl_4 or KBr pellets). Reagent-grade solvents and freshly distilled pyridine were used; column chromatography was carried out on Silica gel 60 (0.040—0.063 mm; Merck). Methyl triphenylphosphoranylideneacetate (**3b**) (Acros) was used as purchased; pyridinium methoxycarbonyl(phenyl)methylide (**6**) was generated from methyl bromophenylacetate according to a standard procedure.[3] The cyclopropyldiazonium salt was prepared from *N*-cyclopropyl-*N*-nitrosourea as described earlier.[10,11]

Dimethyl 3-methoxycarbonyl-2-(triphenylphosphoranylidene)-4,5-diazahept-5-ene-1,7-dioate (7b). A mixture of methyl triphenylphosphoranylideneacetate (**3b**) (12.5 g, 37.4 mmol) and methyl diazoacetate (1.96 g, 19.6 mmol) in chloroform (25 mL) was kept at 20 °C for 12—14 days until the starting ylide was consumed (^1H NMR data). Then the solvent was removed *in vacuo* (bath temperature not above 30 °C) and the residue was dissolved in ether and cooled to 0 °C. The resulting oil was crystallized from benzene to give compound **7b** (2.79 g) as a colorless crystalline solid, m.p. 164—166 °C (decomp.). An additional crop (5.41 g) was obtained by mixing the ethereal solution with an equal volume of hexane and cooling. The total yield of ylide **7b** was 87%. Found (%): C, 64.28; H, 5.50; P, 5.98. $C_{27}H_{27}N_2O_6P$. Calculated (%): C, 64.03; H 5.37; P, 6.12. Partial MS (EI), *m/z* (I_{rel} (%)): 447 (8) $[M - CO_2Me]^+$, 405 (14), 262 (18) $[PPh_3]^+$, 59 (100) $[CO_2Me]^+$. ^{1}H NMR ($CDCl_3$, 25 °C), δ: 3.15 and 3.56 (both s, 3 H (~2 : 1), COOMe at the ylide C atom); 3.72 (s, 6 H, 2 OMe); 4.18 (m, 1 H, CH); 6.60 and 6.75 (both s, 1 H (~1 : 2), CH); 7.61 (m, 16 H, 3 Ph and NH). ^{1}H NMR ($CDCl_3$, 50 °C), δ: 3.28 (br.s, 3 H, COOMe at the ylide C atom); 3.71 (s, 6 H, 2 OMe); 4.19 (dd, 1 H, CH, $^3J_{H,H}$ = 7.3 Hz, $J_{H,P}$ = 16.4 Hz); 6.70 (s, 1 H, CH); 7.61 (m, 16 H, 3 Ph and NH). ^{13}C NMR ($CDCl_3$), δ: 42.5 (d, ylide C atom, $J_{C,P}$ = 126 Hz); 49.2 (COO$\underline{Me}$ at the ylide C atom); 51.4 and 52.2 (2 OMe); 61.1 (d, CH, $J_{C,P}$ = 16.1 Hz); 126.2 (d, Ph(C_{ipso}), $J_{C,P}$ = 91.5 Hz); 128.7 (d, Ph(C_o), $J_{C,P}$ = 12.8 Hz); 132.2 (d, Ph(C_p), $J_{C,P}$ = 3.2 Hz); 133.7 (d, Ph(C_m), $J_{C,P}$ = 9.6 Hz); 165.1 (C=N); 169.7 and 170.0 (2 COO); 173.1 (d, COO at the ylide C atom, $J_{C,P}$ = 8.0 Hz). ^{31}P NMR ($CDCl_3$, 25 °C), δ: 22.4 and 23.5.

3,4,5-Tri(methoxycarbonyl)-2-pyrazoline (8). Ylide **7b** (0.50 g, 1 mmol) was refluxed in $CHCl_3$ (10 mL) for 6 h. Then the solvent was removed and the residue was purified by column chromatography on silica gel with hexane—AcOEt (4 : 1) as an eluent. The pyrazoline **8** obtained (0.22 g, 93%) was identical with a sample prepared[1] from methyl diazoacetate and methyl fumarate.

Dimethyl 5-methoxycarbonyl-2,6-diphenyl-3,4-diazahepta-2,5-diene-1,7-dioate (13). Potassium carbonate (6.90 g, 0.05 mol) was added to a mixture of *N*-[α-(methoxycarbonyl)benzyl]pyridinium bromide (1.85 g, 6 mmol) and methyl diazoacetate (0.60 g, 6 mmol) in acetonitrile (25 mL). The reaction mixture was stirred for 18 h and then diluted with water (50 mL). The product was extracted with CH_2Cl_2 (50 mL). The organic layer was separated, dried with Na_2SO_4, and concentrated *in vacuo* to give a dark brown solid (~2.0 g). Column chromatography of this solid on silica gel with benzene as an eluent gave compound **13** (0.36 g, 60%) as colorless crystals, m.p. 129—131 °C, R_f 0.20 (benzene). Found (%): C, 63.88; H, 5.11; N, 6.96. $C_{21}H_{20}N_2O_6$. Calculated (%): C, 63.63; H, 5.09; N, 7.07. Partial MS (EI), *m/z* (I_{rel} (%)): 396 (58) $[M]^+$, 77 (100). ^{1}H NMR ($CDCl_3$, 25 °C), δ: 3.50, 3.78 and 3.98 (all s, 3 H each, 3 OMe); 7.30 and 7.58 (both m, 8 H and 2 H, 2 Ph); 14.10 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 52.3, 52.4 and 52.7 (OMe); 127.7, 128.0, 128.1, 128.5, 128.8 and 131.0 (Ph(CH)); 130.2 and 134.5 (Ph(C)); 134.1 and 135.0 (C=C); 149.6 (C=N); 162.6, 163.5 and 168.6 (COO).

Methyl cyclopropylazo(triphenylphosphoranylidene)acetate (14). Potassium carbonate (3.14 g, 22 mmol) was added at 5—7 °C to a mixture of methyl triphenylphosphoranylideneacetate (1.52 g, 4.5 mmol) and *N*-cyclopropyl-*N*-nitrosourea (1.47 g, 11 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was vigorously stirred for 3 h and filtered. The solvent was removed *in vacuo* and the residue was recrystallized from AcOEt to give azo adduct **14** (1.42 g, 78%) as yellow crystals, m.p. 184—185 °C. Found (%): C, 71.32; H, 5.52; P, 7.48. $C_{24}H_{23}N_2O_2P$. Calculated (%): C, 71.63; H 5.76; P, 7.70. Partial MS (EI), *m/z* (I_{rel} (%)): 402 (0.6) $[M]^+$, 401 (0.8) $[M - H]^+$, 262 (100), 183 (28). ^{1}H NMR ($CDCl_3$), δ: –0.04 and 0.45 (both m, 2 H each, CH_2CH_2); 3.08 (m, 1 H, CH); 3.66 (s, 3 H, OMe); 7.41 and 7.52 (both m, 6 H and 9 H, 3 Ph). ^{13}C NMR ($CDCl_3$), δ: 6.2 (CH_2CH_2); 45.5 (CH); 50.5 (OMe); 84.9 (d, ylide C atom, $J_{C,P}$ = 105 Hz); 125.6 (d, Ph(C_{ipso}), $J_{C,P}$ = 91.9 Hz); 128.3 (d, Ph(C_o), $J_{C,P}$ = 12.6 Hz); 131.6 (d, Ph(C_p), $J_{C,P}$ = 2.9 Hz); 133.5 (d, Ph(C_m), $J_{C,P}$ = 9.8 Hz); 167.6 (d, OCO, $J_{C,P}$ = 32.0 Hz). ^{31}P NMR ($CDCl_3$), δ: 9.6.

5-Chloro-1-cyclopropyl-6-oxo-3-(triphenylphosphonio)-1,6-dihydropyridazin-4-olate (16a). A solution of chloroacetyl chloride (0.074 g, 0.66 mmol) in CH_2Cl_2 (1 mL) was added at 15 °C to a solution of ylide **14** (0.22 g, 0.55 mmol) in CH_2Cl_2 (3 mL) and triethylamine (0.11 mL, 0.86 mmol). The reaction mixture was kept for 24 h and treated with water (10 mL). The organic layer was separated, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The dark residue was separated by preparative TLC on SiO_2 with MeOH—$CHCl_3$ (1 : 15) as an eluent, R_f 0.28. The yield of dihydropyridazine **16a** was 0.16 g (65%), beige crystals, m.p. 257—259 °C. Found (%): C, 66.94; H, 4.39; Cl, 7.80; P, 6.78. $C_{25}H_{20}ClN_2O_2P$. Calculated (%): C, 67.19; H, 4.51; Cl, 7.93; P, 6.93. Partial MS (ESI, $CHCl_3$—MeOH), *m/z* (I_{rel} (%)): 447 (15) $[M + H]^+$, 469 (100) $[M + Na]^+$, 915 (80) $[2 M + Na]^+$ (these values refer to ^{35}Cl). ^{1}H NMR ($CDCl_3$), δ: 0.54 and 0.76 (both m, 2 H each, CH_2CH_2); 4.19 (tt, 1 H, CH, J_{cis} = 7.6 Hz, J_{trans} = 3.9 Hz); 7.55—7.78 (m, 15 H, 3 Ph). ^{13}C NMR ($CDCl_3$), δ: 5.9 (CH_2CH_2); 33.1 (CH); 109.3 (d, C(5), $J_{C,P}$ = 15.3 Hz); 119.1 (d, Ph(C_{ipso}), $J_{C,P}$ = 92.1 Hz); 128.9 (d, C(3), $J_{C,P}$ = 124 Hz); 129.5 (d, Ph(C_o), $J_{C,P}$ = 12.9 Hz); 134.3 (Ph(C_p)); 134.5 (d, Ph(C_m), $J_{C,P}$ = 9.8 Hz); 160.6 (C(6)); 164.4 (d, C(4), $J_{C,P}$ = 16.1 Hz). ^{31}P NMR ($CDCl_3$), δ: 20.9.

1-Cyclopropyl-6-oxo-5-phenyl-3-(triphenylphosphonio)-1,6-dihydropyridazin-4-olate (16b). A solution of phenylacetyl chloride (0.067 g, 0.43 mmol) in CH_2Cl_2 (1 mL) was added to a solution of ylide **14** (0.145 g, 0.36 mmol) and triethylamine (0.08 mL, 0.56 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was kept at 18 °C for 2 days and then treated with water (10 mL). The organic layer was separated and dried with anhydrous Na_2SO_4. The dark residue was separated by preparative TLC on SiO_2 with MeOH—$CHCl_3$ (1 : 15) as an eluent, R_f 0.30. The yield of dihydropyridazine **16b** was 0.10 g (57%), yellow crystals, m.p. 258—260 °C. Found (%): C, 76.03; H, 5.03; P, 6.18. $C_{31}H_{25}N_2O_2P$. Calculated (%): C, 76.22; H 5.03; P, 6.34. Partial MS (ESI, MeCN), *m/z* (I_{rel} (%)): 489 (100) $[M + H]^+$, 511 (18) $[M + Na]^+$, 999 (28) $[2 M + Na]^+$. ^{1}H NMR ($CDCl_3$), δ: 0.56 and 0.78 (both m, 2 H each, CH_2CH_2); 4.18 (tt, 1 H, CH, J_{cis} = 7.4 Hz, J_{trans} = 4.0 Hz); 7.12 (tt, 1 H, Ph(H_p), ^3J = 7.0 Hz, ^4J = 1.4 Hz); 7.31 (tt, 1 H, Ph(H_m), ^3J = 7.0 Hz, ^4J = 1.5 Hz); 7.57—7.78 (m, 15 H, 3 Ph); 7.97 (dd, 1 H, Ph(H_o), ^3J = 7.0 Hz, ^4J = 1.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 5.6 (CH_2CH_2); 32.7 (CH); 112.3 (d, C(5), $J_{C,P}$ = 9.2 Hz); 120.1 (d, Ph(C_{ipso}), $J_{C,P}$ = 92.2 Hz); 125.5 (Ph(C_p)); 127.0 (Ph(C_m)); 129.3 (d, Ph(C_o), $J_{C,P}$ = 13.0 Hz); 130.2 (Ph(C_o)); 130.6 (d, C(3), $J_{C,P}$ = 118 Hz); 131.8 (Ph(C_{ipso})); 133.8 (Ph(C_p)); 134.2 (d, Ph(C_m), $J_{C,P}$ = 10.2 Hz); 162.7 (C(6)); 166.8 (d, C(4), $J_{C,P}$ = 15.2 Hz). ^{31}P NMR ($CDCl_3$), δ: 20.8.

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